THE
PREPARATION AND PROPERTIES
OF
PURE HYDROGEN PEROXIDE

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A Thesis

-by

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PREPARATION AND PROPERTIES OF HYDROGEN PEROXIDE

TABLE OF CONTENTS

SECTION 1.

Page

General Introduction

TABLE OF CONTENTS

SECTION 11

The dielectric constant of water, peroxide and its Aqueous Solutions.

Page

The Debye Equation

Table of Contents (Page 2, continued)

TABLE OF CONTENTS

SECTION 111

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THE PREPARATION AND PROPERTIES OF HYDROGEN PEROXIDE.

General Introduction.

A casual glance through the literature makes at once evident the variety of uses aqueous Solutions of Hydrogen Peroxide are capable of. Its bleaching power, energetic oxidizing properties and antiseptic action make it an important chemical compound to applied Science.

From the standpoint of pure science its interest lies both in the similarities and distinguishing characteristics to water. Owing to the value attached to all the properties of water it is extremely important to study a compound whose properties more nearly approximate to water than any other substance we at present know.

Probably the two most distinguishing characteristics are those of instability and oxidizing properties both of which properties appear to be attributable to the same cause, the loose combination of an extra Oxygen atom to an extremely stable molecule, water.

The purpose of this thesis then is to measure those physical constants of the substance which would enable a just comparison to be made between the constants already known for water and those determined for peroxide.

As the criterion of purity the melting point has been redetermined and found to be slightly different from that formerly found.. The state of aggregation of the molecules of Peroxide has been tested from the standpoint of the distribution Law and qualitatively verified by a subsequent Dielectric Constant determination of aqueous Solutions and pure Hydrogen Peroxide.

Finally by means of a specially designed conductivity apparatus making use of a quadrant electrometer, the conductivity of weak and strong electrolytes have produced evidence as to the ionizing power of the substance as compared to water.

Historical Introduction

The term "eau oxygènée" applied to designate what we now call Hydrogen Peroxide is singularly appropriate. L. J. Thenard ① first described the compound in 1818 in a paper entitled "Observations Sur la Combinaisons entre l'Oxygenée et Divers Acides". The discovery was made while Thenard was investigating the action of sulphuric, nitric, arsenic, phosphoric and acetic acids on barium peroxide. His first supposition was that the liquids he obtained were "produits suroxygènées" of the various acids but later he definitely showed that the liquids were in every case a super oxide of hydrogen. He correctly endowed this compound with energetic oxidizing power and showed that under the influence of heat the compound decomposed giving rise to water and oxygen.

Natural Occurrence.

There is a certain amount of uncertainty about the alleged presence of hydrogen peroxide in the atmosphere and rain, snow and dew. C.F. Schonbein, E. Schone[2] and others claim having detected its presence in the atmosphere and rain water. Other investigators, in particular A. Houleau and L. I. de N. Ilsova[3] deny its existence. In any case the amount must be very small - between 0.04 and 1 mgrm per litre of rain water. In a year's observation at Moscow, E. Schone reported 110 mgrm of peroxide in the rain and snow which fell per square metre.

According to A. Bach,[4] when the chlorophyll of plants acts on carbon dioxide and water in sunlight, formaldehyde CH_2O, percarbonic acid H_2CO_4 are formed, as indicated by the following equation $3H_2CO_3 \rightarrow 2H_2CO_4 + CH_2O$. The percarbonic acid breaking down into CO_2 and peroxide, thus, $H_2CO_4 \longrightarrow CO_2 + H_2O_2$. The ultimate products are of course CO_2 H_2O and O_2 due to the decomposition of the peroxide formed. A great many investigations tend to show the possibility of hydrogen peroxide being an intermediate compound in many natural processes. Due, however, to its case of decomposition its presence is more often assumed than proved.

The Formation of Hydrogen Peroxide.

(1) Formation of Hydrogen Peroxide by Action of Heat.

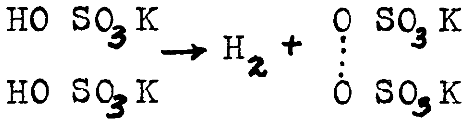
H_2O_2 can be formed by passing a current of moist O_2 through a tube at 2000°C. and rapidly chilling the hot gases. W. Nernst has estimated the percentage H_2O_2 capable of existing in equilibrium with water and O_2 at 1/10 atmospheres pressure to be quite small i.e. at 2500°C. .66%, , at 650°C. .00036%. It is perfectly obvious that if the hydrogen peroxide formed at the high temperature is to survive, cooling must be very rapid.

(2) Formation of Hydrogen Peroxide by Exposure to Ultra Violet Radiations.

Water confined in a quartz vessel is decomposed by rays from a mercury lamp. The reaction may be represented as follows $2H_2O = H_2O \underset{V}{+} H_2$, of course the hydrogen peroxide is subsequently decomposed to give water and O_2 and after sufficient length of time has elapsed the hydrogen and oxygen evolved by both of these reactions are in the proportions which would occur if water were directly decomposed into its elements.

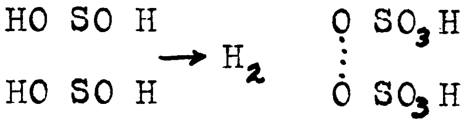
(3) Formation of Hydrogen Peroxide by Electrolysis.

The soln which collects around the anode during the electrolysis of slightly acidulated water (the acid in question being H_2SO_4) possesses oxidizing properties usually assumed to be due to hydrogen peroxide. The mechanism of such a reaction may be something of the following nature. According to Caven & Lanler[5] potassium persulphate may be obtained at the anode using a high current density from the electrolysis of potassium acid sulphate, thus -



$$\begin{matrix} HO\ SO_3K \\ HO\ SO_3K \end{matrix} \rightarrow H_2 + \begin{matrix} O\ SO_3K \\ \vdots \\ O\ SO_3K \end{matrix}$$

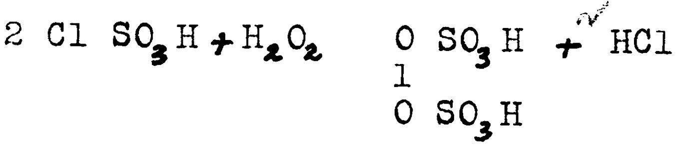
It would seem probable that the production of hydrogen peroxide at the anode with water slightly acidulated with H_2SO_4 would conform to the following scheme



$$\begin{matrix} HO\ SO\ H \\ HO\ SO\ H \end{matrix} \rightarrow H_2 \quad \begin{matrix} O\ SO_3H \\ \vdots \\ O\ SO_3H \end{matrix}$$

The per sulphuric acid then reacts with water to give $H_2S_2O_8$ $H_2O \rightarrow H_2O_2 + H_2S_2O_7$ as an intermediate product.and then the reaction ultimately gives $H_2O_2 + H_2S_2O_7 \rightarrow 2H_2SO_4 + O$.

Probably it is worth noting in this connection that chlorosulphonic acid presumably reacts with anhydrous hydrogen peroxide according to the scheme (5)



$$2\ Cl\ SO_3H + H_2O_2 \quad \begin{matrix} O\ SO_3H \\ 1 \\ O\ SO_3H \end{matrix} + 2HCl$$

From this reaction it is evident that persulphuric acid can be considered as a derivative of hydrogen peroxide in the following manner

$O\ H$
1 becomes on substitution of the SO_3H
$O\ H$ groups for the two H atoms.

$O\ SO_3H$
1 per sulphuric acid.
$O\ SO_3H$

Commercial Preparation of H_2O_2

One of the modern methods takes advantage of one of the reactions above mentioned. An aqueous solution of either potassium persulphate or persulphuric acid is electrolysed using a high current density with the subsequent production of a fairly pure product containing about 30% hydrogen peroxide by weight.

Nature of the Impurities usually present in the Commercial Product.

Before the commercial product can be used for any sort of investigation it must be purified. Obviously if we know what the impurities are we stand a much better chance of removing them. Usually suspended and dissolved inorganic solids, traces of salts of heavy metals together with a small percentage of sulphuric acid form the most important ones. Due, however, to the instability of the commercial product the manufacturer usually adds what is termed an inhibitor or more correctly an anticatalyst. This added material which tends to prevent the decomposition may be any of a variety of substances; alcohol, glycerol, ether, napthalene, sodium pyrophosphate, oxalic acid, pyrogallol, acetanilide, magnesium silicate and salicyclic acid are all used.

Chemical Effects of the Inhibitors on Peroxide.

In the case of organic inhibitors actual chemical oxidation may often take place. It is not an uncommon thing to notice the smell of nitrobenzene from peroxide solutions to which acetanilide has been added. First of all Hydrolysis of the acetanilide occurs $CH_3CONH\,C_6H_5 \rightarrow CH_3COOH + C_6H_5NH_2$.

The aniline is then slowly oxidized to nitrobenzene according to the following scheme -

$$C_6H_5NH_2\;\underset{O}{}\;{}_2HNC_6H_5 \rightarrow C_6H_5NH.NH\;C_6H_5$$

Hydrazobenzene

$$C_6H_5N:\;N\;C_6H_5 \xrightarrow{O} C_6H_5\underset{\underset{O}{\smile}}{N\;\;N}\;C_6H_5 \rightarrow$$

Azobenzene Azoxybenzene

2 $C_6H_5NO_2$ which is nitrobenzene.

Another example is salicyclic acid. This is apparently added as sodium salicylate but becomes hydrolysed to salicyclic acid. Because then of the energetic oxidation of the peroxide the inhibitor originally added is not necessarily the substance found in the solution due, as has been shown, to chemical reaction.

Partial Inhibition of the Decomposition of Hydrogen Peroxide or Negative Catalysis.

As has been mentioned previously there are a large number of substances classified broadly as organic and inorganic which inhibit to a considerable extent the decomposition of hydrogen peroxide. The effect then is a typical example of the important phenomenon known as "Negative Catalysis". 6

Unfortunately in contrast to the marked attention and copious literature devoted to positive catalysis, no well defined opinion is prevalent as to causes or, in some cases, even the existence of negative catalysis. Its importance however from both the standpoint of chemical theory and applied chemistry in such problems as decomposition of hydrogen peroxide (thermal and Photochemical) halogenation and autoxidation warrant a detailed consideration.

As in discussion of positive catalysis one can classify negative catalysis as either homogeneous or heterogeneous according to whether one or more than one phase is concerned in the reaction.

Ordinarily the latter type is explained on the assumption of interaction with, or absorption of the negative catalyst on the positive catalyst. Undoubtedly many instances of "poisoning" must be attributed to such a cause. If the positive catalyst be a colloid the negative one may act as an agglomerating agent thereby considerably varying the interfacial surface.

Retardation in homogeneous media does not appear to be so readily explained on this basis. In this case the explanation seems to be in one, or both of the following considerations, Titoff,[7] as a result of his work on the oxidation of sodium sulphite solutions in presence of various catalysts and inhibitors, concluded that in this case negative catalysis consisted in the suppression of the positive catalytic activity.

There appears to be however quite a large number of cases which do not conform to Titoff's point of view. It seems necessary to find some other explanations for the inhibition of the autoxidation of benzaldehyde, styroline, oils, fats, etc., which has been carefully carried out by Moureu and Dufraisse.[8]

The relatively small amounts of inhibitor excite attention Accordingly to Moureu and Dufraisse, a trace of hydroquinone can suppress the oxidation of benzaldehyde. The question now arises how can one molecule of an inhibitor in say, 10000 molecules of reacting substance so markedly affect the process of such an easily oxidizable substance as benzaldehyde. The human impossibility of being in two places at the one time makes it inconceivable how any one molecule could be 10000 places at the same time. A simple calculation, however, will indicate that the idea is not really absurd. Moureu found that carefully purified benzaldehyde absorbed two cubic centimeters of oxygen per minute. The same amount of benzaldehyde containing .005 grams of hydroquinone absorbed less than .005 cubic centimeters of oxygen.

This permits us to calculate that the number of benzaldehyde molecules reacting per minute is approximately 5 x 10^{19}, also .005 grams of hydroquinone represents 3 x 10^{19} molecules. It would, therefore, appear from this calculation that there are a sufficient number of hydroquinone molecules to form an equimolecular compound with all the benzaldehyde molecules normally reacting per one half minute. Now compound formation proceeds at an exceedingly rapid rate relative to the benzaldehyde-benzoic acid reaction so that there are an adequate number of hydroquinone molecules to react in stoicheiometrically simple ratios with the molecules which would normally have reacted in the same time interval.

With the point of view of compound formation on the one hand and suppression of the positive catalyst on the other we are in a position to discuss the inhibition of the decomposition of hydrogen peroxide. For this purpose we may choose a specific case - viz. the negative catalytic action of acetanilide.

First of all by making use of two justifiable assumptions let us calculate whether^"compound formation" theory is probable. The first assumption is that the decomposition of ordinary 3% hydrogen peroxide of commerce decomposes at the rate of about 1/2% per day, i.e., .001 gram per minute. The number of peroxide molecules decomposing per minute would be $\frac{.0001}{34} \times 6.06 \times 10^{23} = 2 \times 10^{19}$, add one tenth gram of acetanilide per litre we have $\frac{.1}{135} \times 6.06 \times 10^{23}$ 4.5×10^{20}. Evidently there are more than sufficient number of acetanilide molecules to form a compound of the formulae $H_2O_2 \cdot CH_3CONH\ C_6H_5$ which due to its rapidity takes priority over the slower reaction leading to water and oxygen.

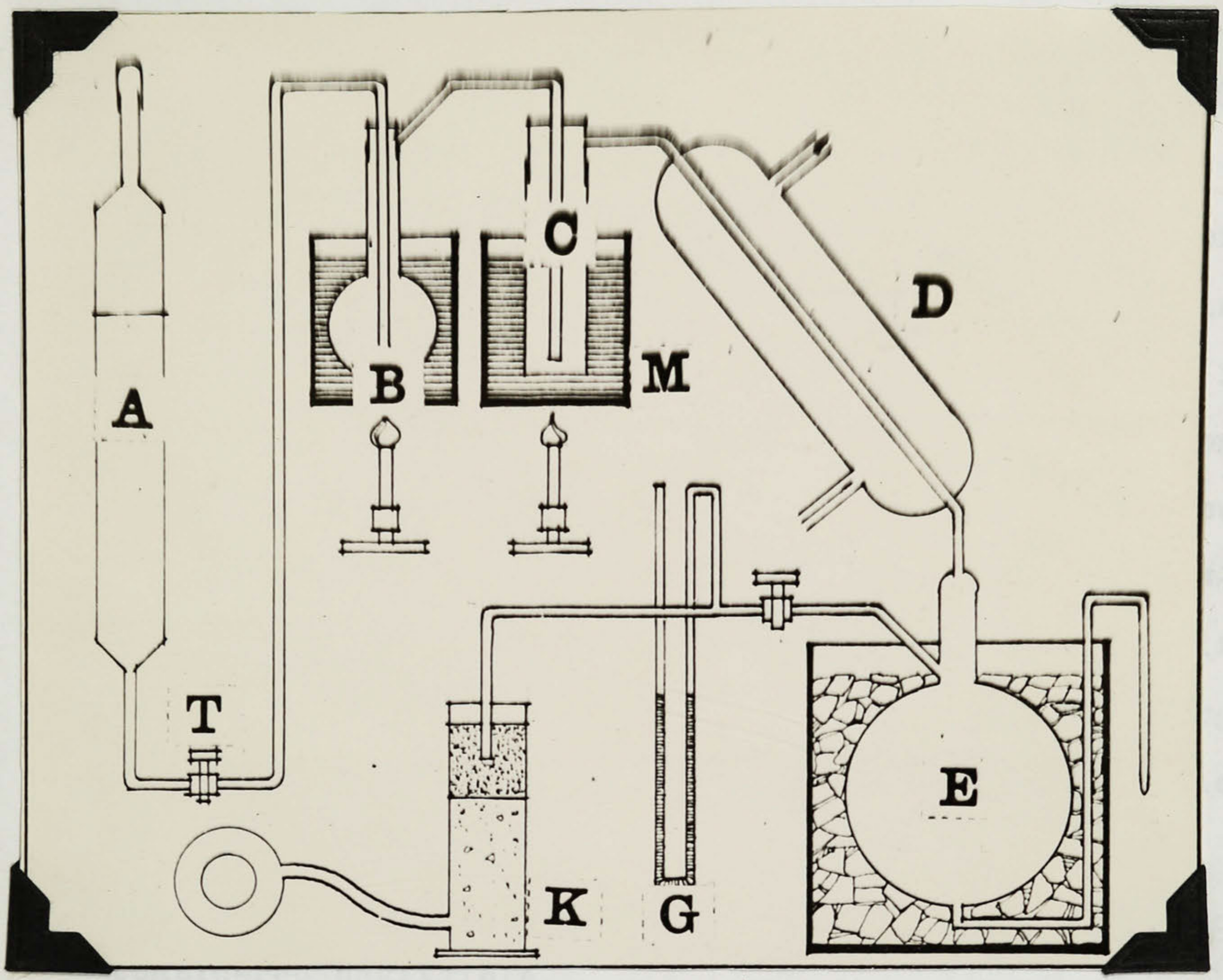
We have just shown on the basis of the calculation that the compound formation is probable. Let us now compare it with the conception of the suppression of a positive catalyst.

It is to be noted the phrase "hydrogen peroxide of commerce" was used above. If the same product be carefully purified, by a method to be described later and so far as it is possible to determine free from any inhibitor, decomposition appears to be negligible . The logical consequence of this experimental fact then, would appear to be that the reaction under ordinary circumstances is due to a positive catalyst and that the acetanilide suppresses this catalyst to some extent. The formulation of a mechanism appears to be quite impossible because of the number of variable factors involved. All that one can say about these two theories in this specific instance is that suppression of a positive catalyst appears to fit in best with experimental facts.

The Preparation of Pure Aqueous Solutions of Hydrogen Peroxide and also Pure Hydrogen Peroxide.

Description of Apparatus.

Essentially the apparatus is that commonly used in vacuum distillations. The receptacle A is separated from the rest of the apparatus by an ungreased tap T and serves as a container for the peroxide prior to its entering the distilling flask B. This distilling flask is fitted to the apparatus by means of an accurately ground glass joint. The flask is firmly held in position by means of the water bath M surrounding the main body of the distilling flask. The trap C is likewise fitted through a ground glass joint and prevents anything that might be mechanically carried over from the distilling flask reaching the distillate. The vapour is cooled by a condenser D and collected in a two litre receiver E. This receiver is packed in a freezing mixture of ice and salt. A tube H is connected to a manometer G, then to a calcium chloride manganese dioxide trap K to a cenco pump. One of the important factors in obtaining the highest efficiency is to have an adequate cooling system. A condenser about five (5) feet long through which water at about 3-5°C. is rapidly passing has been found quite efficient. The trap H consisted of a tube about two (2) inches in diameter and a foot long. It was filled about 3/4 full of quite finely divided calcium chloride on top of which was placed a layer of manganese dioxide. The function of this was to decompose any hydrogen peroxide into water and oxygen, the calcium chloride in turn removing the water. It was repeatedly observed, however, that only a small amount



Distillation apparatus for the preparation of pure aqueous solutions of hydrogen peroxide.

A. Reservoir capacity 500 c.c.
T. Ungreased tap surrounded by a water bath to prevent leakages
B. Distilling flask surrounded by water bath. Temp.80°C
C. Trap surrounded by water bath M.temp. 80°C
D. Water condenser
E. 2 litre flask surrounded by ice and salt.
G. Manometer
K. Manganese, dioxide, Calcium chloride trap

of water vapour was carried over from the receiver. At least twelve (12) litres of peroxide can be distilled before the calcium chloride appears moist. It was further observed that upon removal of the oil from the pump on two different occasions no signs of rusting or corrosion could be detected in the mechanism.

Preparation for and process of Distillation.

For this purpose the 30% commercial hydrogen peroxide is used. As previously mentioned this contains impurities which the subsequent process of distillation is intended to remove. Stated briefly two classes of impurities exist - organic and inorganic. An efficient vacuum distillation must accomplish two purposes - a pure distillate without heavy losses of peroxide. No difficult problem is met with in the case of the removal of inorganic materials because any that are present are non-volatile or at least as in the case of sulphuric acid its vapour pressure at the temperature considered is low enough to be considered negligible.

Actually the reverse is true where organic compounds are concerned especially those which exert a preservative action on the peroxide. Consequently depending on the nature of the substance present the technique involved in the distillation must be altered. The first problem obviously must be to determine what the inhibitor is. This is in many cases not an easy task for two reasons - firstly the concentration is small and secondly identification reactions successful in water are not necessarily indicative in the presence of hydrogen peroxide.

Let us assume one had actually shown the presence of a very commonly used preservative acetanilide. We wish to free the solution from the material. It is well known that at 75°C. this substance readily hydrolyses into aniline and acetic acid, both of which steam distill. Some substance must be added which will form non-volatile compounds with these constituents. One could distill in sulphuric acid first eliminating aniline as aniline sulphate. A second distillation with potassium hydroxide would fix the acetic acid.

In some peroxide recently used the above inhibitor was shown to be absent. There were good reasons to believe this was either sodium salicylate or salicylic acid. Colour reactions known to give good results in aqueous solution were attempted.

The tests however when carried out in the presence of the peroxide were so masked as to make a decision difficult, if not impossible. Some of the peroxide in question had been concentrated and this, when cooled down, resulted in the formation of tiny needle crystals which floated on the surface of the solution. By using a glass filter plate these crystals were removed from the influence of the peroxide and dissolved in a small quantity of water. To a portion of this a few drops of potassium nitrite, acetic acid and copper sulphate were added which, when heated, gave the characteristic test for salicyclic acid, i.e. a blood red solution. This test was considered as confirmatory evidence of the presence of the above mentioned compound. This substance sublimes at 76°C. at ordinary pressure and it also steam distills.

The problem of distillation obviously resolves itself into an efficient method for the removal of not only the inhibitor but the other inorganic impurities as well, AG_2SO_4 was tried. This substance will hold back any chlorides and silver salicylate is also known. The vapour pressure of sulphuric acid is so low that it will introduce no complications. This substance was chosen because it appeared to have no influence on the stability of the peroxide even at 90°C. in vacuo. The distillate gave no test for either sulphates or chlorides but did contain traces of salicylic acid. The preoxide was then distilled in slightly alkaline solution using the following method for determining the meutral condition. Under ordinary conditions for a 30% solution phenolphthalein is not a reliable indicator. To obtain neutrality the following method is recommended 50 C.C. of the solution is diluted to about two (2) litres and, about five (5) drops of phenolpthalein is added. Drop by drop 4 N KOH is let in until the first appearance of a pink colour is evident. The end point so obtained is probably on the alkaline side but just to an extent to prevent undue decomposition and, appears at the same time to be sufficient to prevent the hydrolysis of the potassium salt of salicyclic acid.

Even though the alkali concentration is small, hydrogen peroxide especially at the temperature of distillation is extremely sensitive to it. Further foaming is often noticeable. It was found that both of these difficulties could be eliminated by the simple expedient of adding small quantities of sodium pyrophosphate $NA_2 P_4 O_7$ to the slightly alkaline solution.

The experimental evidence presented would indicate that the correct procedure would be to distill the original, crude product in slightly alkaline solution with a trace of sodium pysophosphate added. This is open to one objection. The quantity of sulphuric acid is quite large 1/2 to 1%. The amount of KOH required is therefore also of considerable magnitude. The first portions to distill deposit the alkali in the flask so that succeeding portions are being distilled, not in slightly alkaline, but quite strongly alkaline solutions. Even therefore if an inhibitor is present, such as sodium pyrophosphate, quite heavy losses are incurred. One might apply the same argument to the double distilled product but it is to be remembered that in this case the sulphuric acid has already been removed and the actual amount of KOH present even at the end of the distillation of 500 c.c. is probably notemore than 10 or 15% of the amount present when the sulphuric neutralization also is required.

When, however, solutions are not required for such experimental work as conductivity or dielectric constant measurements one distillation is probably to be preferred due to the amount of time saved, which, on the whole, may be more important than somewhat larger losses.

Effect of Hydrogen Peroxide on Cenco Pump Oil.

As previously mentioned, vacuum distillation was carried out using an ordinary rotary Cenco pump. It was interesting to find out whether one could detect any change in the physical properties of the pump oil. The most important property from this standpoint appeared to be whether the oil would thicken so as to prevent the proper action of the pump. The obvious constant to be measured in this connection was the viscosity. A sample of the oil was taken and its viscosity determined while another sample was placed in a mechanical shaker with about an equal volume of 30% hydrogen peroxide. The viscosity of the oil was measured using a 20 c.c. pipette The sample which had been shaken with the peroxide was separated and distilled.

Time of Flow of Oil Shaken with H_2O_2 for Five Hours.	Time of Flow of Oil as used ordinarily in Cenco Pump.
118 seconds.	108 Seconds.

All that the experiment attempts to show is that no appreciable change in viscosity takes place under the outlined conditions.

Experimental Procedure.

Concentration.

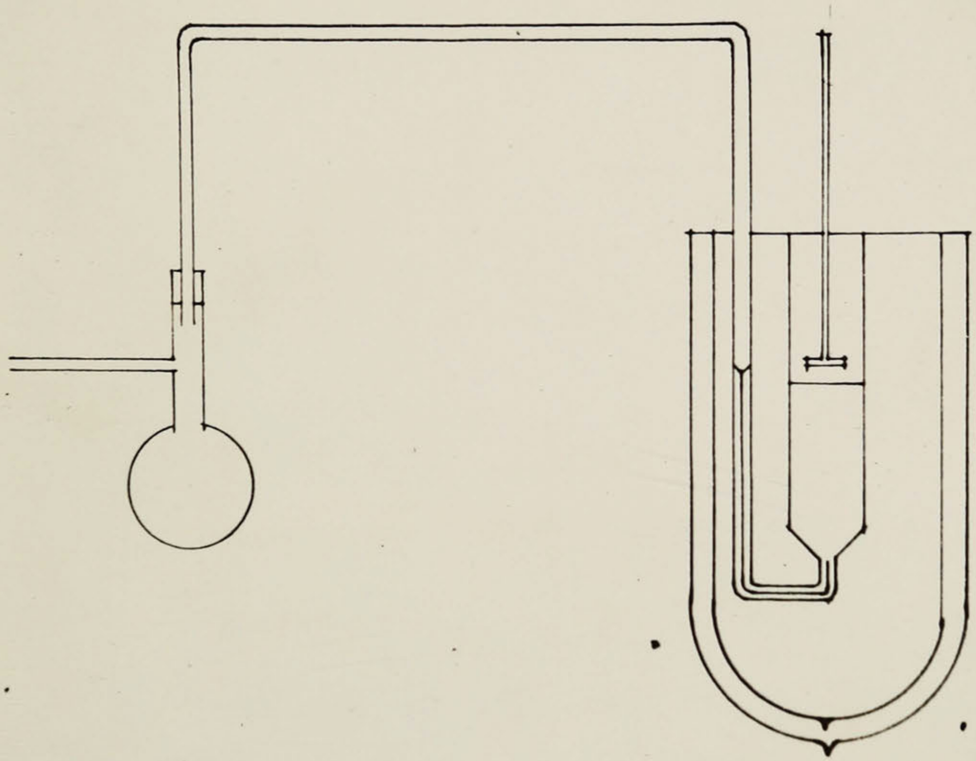
The procedure has been dealt with as to how pure, dilute aqueous solutions of hydrogen peroxide can be obtained. The next step therefore is the concentration. No new difficulties made themselves apparent. The same apparatus carefully cleaned was successfully used. The distilling flask was filled with the dilute solution and the concentration was allowed to go only slowly keeping the temperature at about 40°C. In this way solutions of 90 % strength were obtained. To carry the concentration beyond this point means heavy losses.

Experimental Procedure.

Crystallization.

The only way one can obtain 100% hydrogen peroxide is by the tedious removal of water from the 90% solution obtained in the concentration of the dilute solutions as previously described. The apparatus required is quite simple. The tube used for the crystallization is shown in the diagram and the method is almost self explanatory. To the lower end of the tube a piece of capillary is sealed. The tube was bent through 180° so as to facilitate placing it in the Dewar. Two more right angle bends were then made so that it could be fitted by means of a tight fitting rubber stopper to a distilling flask. A current of air passing through drying towers of calcium chloride and the side arm of the distilling served to stir the peroxide. A cooling bath of carbon dioxide and acetone served to bring the contents of the tube down to a temperature conducive to crystallization. The hydrogen peroxide has a great tendency to supercool but if a temperature of about 25°C. is maintained for a short period of time crystallization will begin without the necessity of seeding. This appears to be an optimum temperature for it was noticed that if the solution was rapidly cooled in a bath of a lower temperature seeding appeared to be almost invariably necessary.

When the mass was about 4/5 solid the tube was quickly raised from the bath and suction applied where the air current for stirring passed. In this way the mother liquor was quickly carried away from the crystals. In order to as completely as possible dry the crystals a glass rod (one end of which was fastened to a disc) served to pack the crystals together and help the process of rapid drying. The process is completed until the value of the permanganate titration indicates within the experimental error complete removal of water.



Crystallisation Apparatus

Usually four crystallizations are sufficient when the original solution is 90% peroxide.

The process of preparation has been briefly described and it is now necessary to consider the preservation of the product.

Preservation of Hydrogen Peroxide.

A great deal has been written about the decomposition of hydrogen peroxide in various containers under various conditions. Under ordinary conditions we will consider glass. There is plenty of experimental evidence to show that soft glass is not an efficient receptacle for peroxide. As is well known soft glass is an alkaline glass and its effect may be due to a thin layer of alkali on its surface. We have, however, had almost complete success with pyrex.

The glass is treated as follows. - A new pyrex container is well washed with distilled water. It is then allowed to stand in contact with strong nitric acid for one or two hours. The flask is thoroughly rinsed with distilled water and dried with a current of air at not higher than 50° The treatment was based on the following arguments. Observation indicated that pyrex was better than soft glass. Alkali rapidly decomposes peroxide. Pyrex, on the other hand, is, if anything, an acid glass. The likelihood was that pyrex would preserve better than soft glass . Obviously the glass must be cleaned with some reagent, cleaning solution was known to have a slight etching action if allowed to stand long enough to secure chemical cleanliness. An etched surface means a larger surface and if decomposition is a surface phenomenon (at least in part) then dichromate-sulphuric mixtures are not to be recommended. The oxidizing acid chosen then was nitric.

It is worth while pointing out here that really pure solutions of peroxide are not unstable. The instability is quite largely due to the presence of foreign substances both in solution and suspension. An observation made will make the reason for this statement clear. A piece of tin was in contact with a solution of peroxide known to contain salicylic acid at a temperature of 0°. After the interval of about five minutes bubbles appeared around the metal surface. The same piece of tin with the same strength of peroxide from which (so far as we were able to ascertain) all salicylic acid was removed showed no tendency to decompose even after a half hour's interval.

It is to be carefully noted that the inference is not to be made that an aqueous solution of the highest purity of hydrogen peroxide will not decompose but rather that a very small trace of a foreign substance appears to enormously accentuate the effect, and where such care has not been taken the results obtained in decomposition experiments may be considered as practically valueless.

Care is also to be taken in confusing catalytic decomposition and actual chemical reaction. An interesting case is that of lead. If a piece of lead is dropped into an aqueous solution a violent reaction occurs. One finds that in this case a large deposit of a lead oxide is actually formed probably PbO_2 and that the violence of the reaction is not that only of a catalytic nature but a chemical compound is actually formed. Grease on a flask will act similarly.

A glass container will preserve peroxide if its surface is free from alkali and it is chemically clean.

The Melting Point of Pure Hydrogen Peroxide.

A permanganate titration was run giving a value of 99.97% peroxide. A Beckmann thermometer was placed in the crystals about 4/5 of the mass being frozen. The value of the mass being - .89 . The freezing point as previously given was taken when complete solidification took place, and the freezing bath was kept at a temperature several degrees below the freezing point of the peroxide. The precaution necessary is to keep the bath .1° below the freezing point continually stirring the liquid. The melting differs from that found by Maass and Hatcher by .90 and this large difference may be ascribed to the slow rate of solidification not taken into account formerly. A carefully corrected reading gave a value of .89°C. The Beckmann thermometer was standardized at 0° . by placing it in supercooled water, freezing same and noting the height the mercury finally rose to.

The Density of H_2O_2 over the whole Temperature Range.

The Dilatometer method was used for this determination. To a bulb of about 6 c.c. capacity, a capillary tube was sealed and a scale from a broken Beckman Thermometer was rigidly fastened to the tube, but of course was so fastened that it could be easily removed for weighing of the tube. A bath of carbon dioxide and ether in an unsilvered Dewar could be kept constant by judicious stirring to 1/10 of one degree and the readings were taken with the aid of a magnifying glass.

The tube was first calibrated with water. Water is preferable as it has the same type of meniscus as peroxide. Water was placed in the tube to a certain height, weighed and the reading on the scale at a definite temperature was noted. Five such readings were deemed sufficient for the purposes of calibration. Knowing the volume of water which could be obtained from the tables from the weight, and also the number of scale divisions corresponding to these volumes the volume of one scale division is obtained, and is equal to ,001515 c.c.

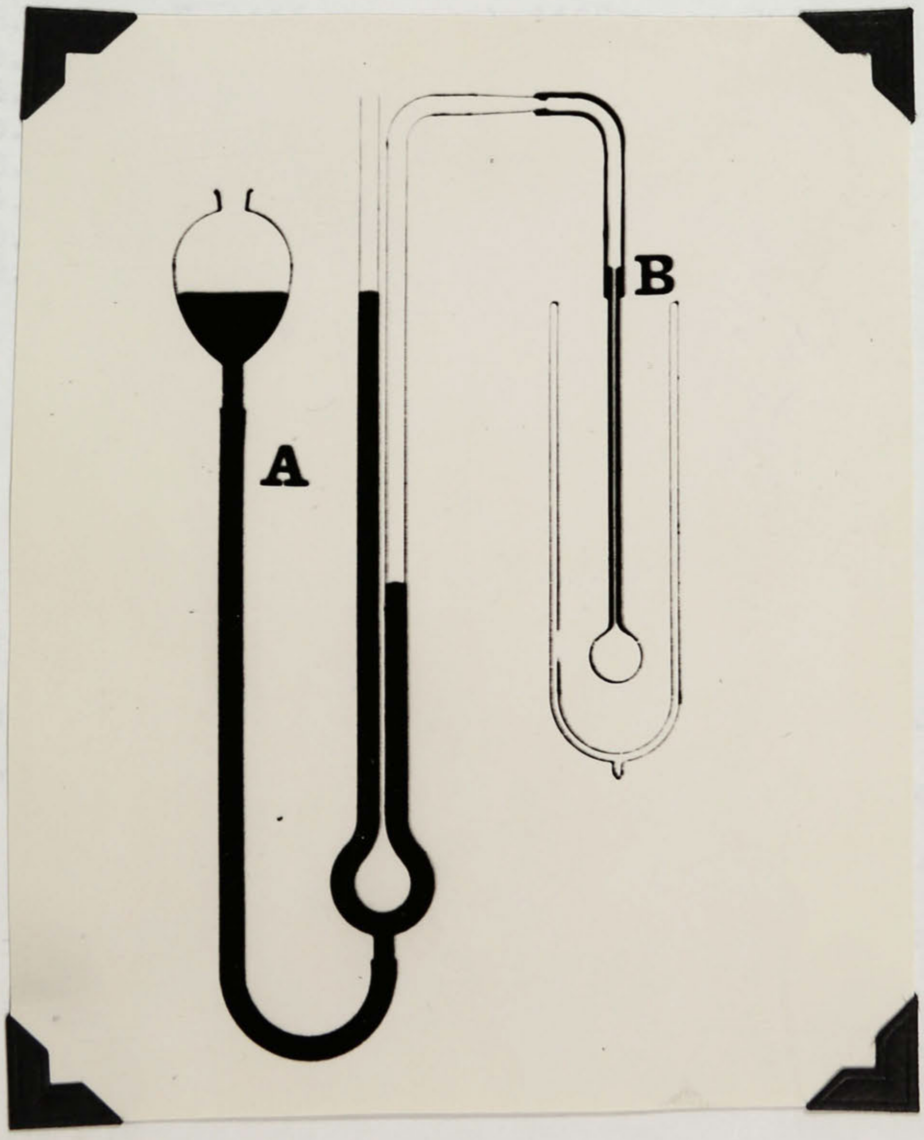
The first attempt to accurately determine the density was most unsuccessful, The dilatometer was made of soft glass and the bulb was blown on the end of the capillary tube. It was only a moment after the peroxide has been placed in the dilatometer that decomposition made itself apparent to a very marked degree. As the tube had been very carefully cleaned the decomposition appears to be due entirely to the glass surface.

Pyrex was then substituted and it was found the decomposition could be considerably reduced especially when tubing of the required size was sealed to the capillary tube, rather than blowing a bulb, as it appeared blowing a bulb strains the glass. A certain amount of local decompsoition is probably due to point surfaces. Hydrofluoric acid was run in and run out again as quickly as possible in order to remove any points without actually etching the glass. It is difficult to say how successful the method is and until more experiments are carried out it is not to be recommended.

It must not be overlooked, however, that the actual volume of gas is small. So far as a capillary tube is is concerned it will nevertheless introduce a serious error in a reading. The decomposition is so slight relative to the weight of the peroxide that over a period of 2 hours no change was noted in the weight.

The following method was used which (as will be shown subsequently) was checked by actually measuring the volume of gas formed. After weighing and attaching the scale the tube was immersed in a carbon dioxide ether bath at 0 C. The tube was allowed to come to the temperature of the bath during which time a slight decomposition took place. The bulb, now at the temperature of the bath, was tapped causing the trapped gas to rise and then the meniscus reading was immediately taken.

The accuracy of this method was proven by the following procedure. The diagram indicates the method.



$$V - \frac{P\ V}{P}\ (R\ -\ R\ )\ K$$

or $$V - (1 - \frac{P}{P}\ (R\ -\ R\ )\ K$$

The values of the density of pure H_2O_2 are given below. The tube was in all cases tapped. A comparison with Dr. Hatcher's figures in included, as well as the calculated values from the equation for the curve.

9

Temperature In C.	Density Experimental	Density Calculated	Difference	Hatcher's Values
-19.7	1.4855	1.4856	.0001	
-13.5	1.4791	1.4791	.0000	
-9.5	1.4744	1.4748	.0004	1.4747
-4.9	1.4701	1.4701	.0000	1.4693
-2.3	1.4669	1.4673	.0004	1.4669
0.0	1.4649	1.4649	.0000	1.4630
2.9	1.4619	1.4619	.0000	1.4596
7.7	1.4569	1.4568	-.0001	1.4547
10.0	1.4543	1.4544	.0001	1.4520
12.4	1.4516	1.4519	.0003	1.4492
14.1	1.4497	1.4500	.0003	1.4476
16.2	1.4475	1.4479	.0004	1.4451
18.0	1.4455	1.4460	.0005	1.4436
20.4	1.4430	1.4435	.0005	
23.3	1.4403	1.4404	.0001	
30.1	1.4331	1.4333	.0002	
32.2	1.4309	1.4311	.0002	
34.0	1.4288	1.4290	.0002	
35.6	1.4273	1.4275	.0002	
39.9	1.4232	1.4231	-.0001	

The equation is $D = 1.4649 + .00105t$

D = density of pure H_2O_2.

t = temperature in °C.

In order to check the accuracy of the density at zero the densities of peroxide solutions at zero were also obtained and in this case the volume of gas was calculated.

The open end of the dilatometer (B) was attached by means of a flexible rubber tubing to one arm of a manometer (A). A reading on the dilatometer scale was taken and, then by raising the mercury level in the other arm the pressure (measured by the difference in height of the two arms) was applied to what bubbles were present.

By means of a formula the volume of the bubbles at atmospheric pressure can be calculated and this volume subtracted from the volume of the liquid at the height the reading under atmospheric pressure was taken. The formula for the calculation of the volume of the bubbles is deduced in the following way.

Let P_1 - atmospheric pressure.

Let P_2 - pressure applied when the mercury level is raised.

Let V_1 - volume of bubbles at pressure P

Let V_2 volume of bubbles at pressure P

Then assuming Bayle's law,

$$P_1 V_1 = P_2 V_2$$

Also $V_1 - V_2 =$ difference in the two readings on the scale x volume of one division

$$V_1 - V_2 = (R_1 - R_2) K.$$

Where R_1 = reading at P_1

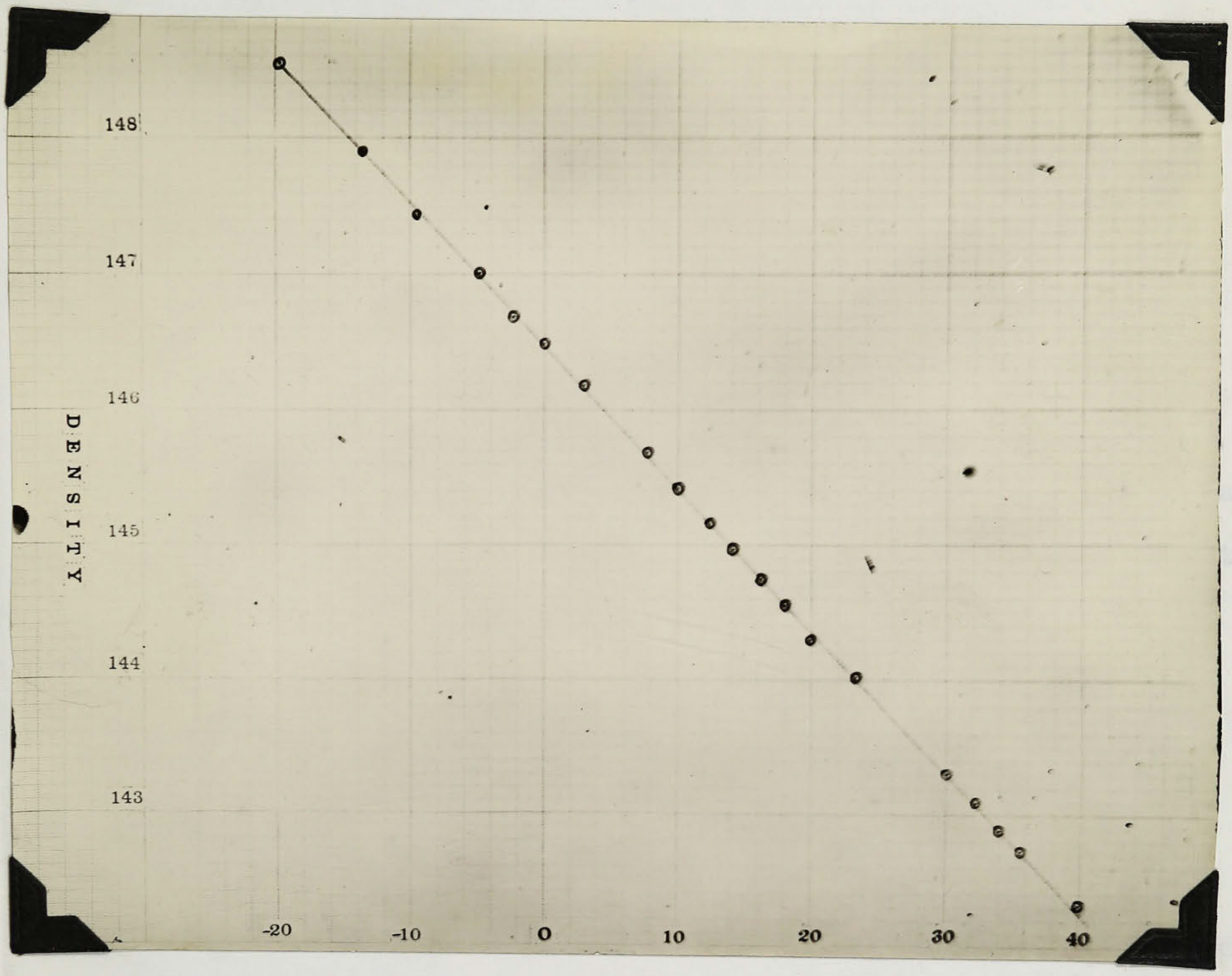
R_2 = reading at P_2

Now $V_2 = \frac{P_1 V_1}{P_2}$ $V_1 = K(R_1 - R_2) \div (1 - \frac{p_1}{p_2})$

by means of the formula above and the necessary corrections applied.

The results are tabulated below.

% H_2O_2	Readings Atmos. Pressure.	Reading P 4 cm.	Density	Volume of gas in c.c.
97.02	96	94	1.4489	.0086
	101	97	1.4486	.0156
	104.5	99	1.4488	.0214
	Mean value for density		1.4488	



The change of the density of pure hydrogen peroxide with temperature.

% H_2O_2 g	Readings Atmos. Pressure.	Reading 124 cm	Density	Volume of gas in c.c.
93.61	267.9	262.5	1.4320	.0211
	268.5	263.0	1.4318	.0215
	270.0	264.1	1.4319	.0235
	Mean value for density		1.4319	

The equation for this curve taking the density at 0°c. for 100 per cent peroxide as 1.4649 is $D = .9486 + .005163A$

D = density

A = % peroxide

The fact that the density of H_2O_2 obtained by merely tapping the tube agrees so far as the curve is concerned with the two values obtained by the 'pressure' method seems to warrant accepting the value at 0° C. correct to at least one part in 7000.

The Distribution Law.

The distribution of H_2O_2 between water and ether.

Before we deal specifically with the above system it is well to consider the significance of the distribution law and what it achieves in quantitatively defining Heterogeneous equilibrium.10

Equilibrium belongs to one of two classes - viz., homogeneous or heterogeneous. The former class lends itself much more readily to either a theorectical or experimental approach. This is due to the fact that the equilibrium is confined to one phase, while the latter, heterogeneous is concerned with two or more. Heterogeneous equilibrium can be defined in two ways. Its qualitative expression is given by the Phase Rule, its quantitative by the Distribution Law, while the former is perfectly general in its scope the latter is extremely limited and may, under the most ideal experimental conditions, only be considered as an approximation to a law - approximation because of the number of variable and unknown factors.

Thermodynamical Deduction of the Distribution Law.

The law can be deduced by means of a thermodynamic cycle carried out at constant temperature. Consider for this purpose two systems at equilibrium and denote them as 1 and 2.

A substance C is distributed between two completely immiscible liquids A and B. Suppose the concentration of C in A and B for system 1 be C_1 and C_2 respectively, and for system 2 C_3 and C_4 respectively. It is then required to show that $\frac{c_1}{c_2} = \frac{c_3}{c_4} =$ Constant.

First Step.

Suppose du molecules of C are taken from A (system 1) and transferred to A system 2. If the process be carried isothermally and reversibly the work done $W_1 = du\ R\ T\ ln\ \frac{c_1}{c_3}$

Second step.

The du molecules transferred to A (system 2) will distribute themselves between A and B. No work is done as equilibrium was assumed to exist.

Third Step

Transfer du molecules from B (system 2) to B (system 1) isothermally and reversibly. The work done $= du\ R\ T\ ln\ \frac{c_4}{c_2} = W_2$.

Fourth Step.

Distribution of the du molecules transferred from B (system 2) will take place but as the system 1 is also assumed to be at equilibrium no work is done.

The work done in carrying out the cycle is therefore

$W_1 + W_2$

i.e. $du\,R\,T\ln\frac{c_1}{c_3} + du\,R\,T\ln\frac{c_4}{c_2} = 0$

i,e. $\frac{c_1}{c_3} = \frac{c_2}{c_4}$ or $\frac{c_1}{c_2} = \frac{c_3}{c_4}$

which was what was to be proved.

Certain assumptions were made that must be noted in obtaining this derivation.

(1) The molecular state of aggregation is the same in both phases for the distributed substances.

(2) The application of the gas law is only justified for very dilute solutions.

(3) The phases are completely immiscible.Despite the limitations imposed on the law the application of it to liquid systems has yielded many usefulfacts and admitted the interpretation of phenomena otherwise inexplicable.

Berthelot and Jungfleish were among the first to note a consistency and constancy in liquid - liquid systems. Their results are interesting in the discussion which will follow and are tabulated below. The partition of Iodine and Bromine between carbon disulphide and water gave the following results.

I_2 in CS_2 & H_2O		K.	Br_2 in CS_2 & H_2O		K.
Grms I_2 per 10 c.c. H_2O.	Grms I_2 per 10 C.C. CS_2		Grms Br_2 per 10 c.c. H_2O.	Grms Br_2 per 10 c.c. CS_2	
.0041	1.74	420	0.176	10.20	58
.0032	1.29	400	0.030	2.46	82
.0016	0.66	410	0.020	1.55	78
.0010	0.41	410	0.0011	0.09	80
.00017	0.076	440			

Three things might be observed in connection with the above results. Especially in the case of iodine the solutions are very dilute, K is not quite constant, the deviations being much larger for Br than for iodine, and lastly the state of aggregation is probably the same in both phases. A more nearly ideal system would be very difficult to obtain than the former of the above and yet quite large deviations are evident.

A great number of systems (the one to be discussed being an excellent example) do not even approximate to a law when the application of the law in its simplest form is applied. Nernst,[12] however, showed that this was, in many cases, due to a lack of consideration of the state of aggregation a distributed substance assumed in each of the two phases. His argument was that the same molecules cannot be in immediate equilibrium if their molecular complexity is different in the two phases.

Let us assume in one of the phases the distributed substance is associated and in the other the molecule is not. We can then deal with the problem by assuming a homogeneous equilibrium in one of the phases and a heterogeneous equilibrium between the non-associated molecules in the two phases. Such an equilibrium could be diagramatically shown -

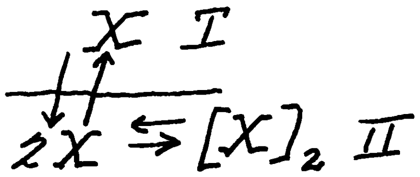
$$X \leftrightarrows [nX \leftrightarrows (X)_n]$$

Nernst's modification then takes the following form.

(1) If the dissolved substances has the same molecular weight in both solvents, its distribution coefficient is independent of the concentration.

(2) If the distributed substance consists of molecules of different molecular complexity the above generalization holds for each molecular species.

We are now in a position to give the mathematical interpretation of this modification of the simple distribution law - the following type of equilibria is assumed.



Let X represent the type of molecule characteristic of both phases and associated in phase 2 to the dimolecular condition. Let C_1 = concentration of molecules as analytically determined in I and C_2- concentration as analytically determined in 2. Let $\overset{a}{A}$ = amount of dissociation of complex molecules into simple.

Then 1 - a = amount of association

Therefore $C_2 a$ = concentration of simple molecules

$C_2(I-a)$ = concentration of complex molecules.

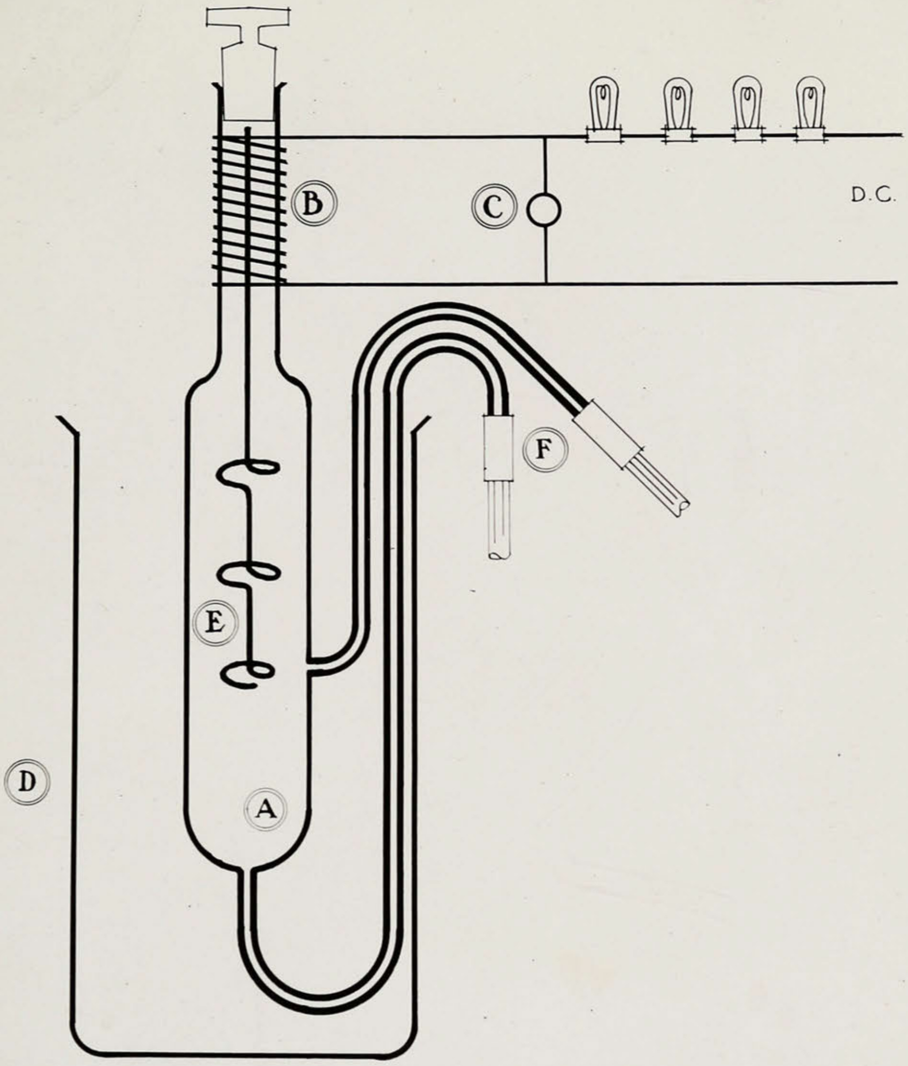
Substituting in the above equilibrium in phase 2 we have -

$$\frac{(C_2 a)^2}{C_2(1-a)} = K_1 \qquad \text{i.e.} \quad C_2 a - \sqrt{C(1-a)K_1}$$

According to Nernst the ratio of the simple molecules in the two phases is constant. We have $\frac{C_1}{C_2 a} - K$ or $\frac{C_1}{\sqrt{C_2(1-a)K_1}} = K_2$

or finally $\frac{C_1}{\sqrt{C_2(1-a)}} = K_3$ = Constant.

To actually define a heterogeneous equilibrium one requires to know the molecular complexity for each and every concentration, that is one must know a.



APPARATUS USED IN DETERMING THE PARTITION COEFICIENTS OF HYDROGEN PEROXIDE BETWEEN ETHER AND WATER

The Distribution of H_2O_2 between Water and Ether.

Bearing the above considerations in mind, let us now consider the actual results obtained and attempt to show how the former points of view fit in with this particular system.

Experimental Procedure.

The apparatus used in this connection was extremely simple, the diagram being almost self-explanatory. Earlier investigators like Walton and Lewis shook a mixture of hydrogen peroxide water and ether in glass stoppered bottles at a constant temperature. This idea was not considered advisable as peroxide shows a distinct tendency to decompose at ground glass surfaces and in order to minimize this difficulty an entirely different idea was used.

A glass tube (A) about 16 cm. long and 2.5 cm. in diameter was drawn out to the diameter of the neck of a 250 c.c. graduated flask. This neck was sealed on providing a means of having the tube closed with a tightly fitted glass stopper. At the bottom and about 2 cm. from the bottom capillary tubes (F) were sealed in the tube (A). Before the bottom was sealed a glass stirrer was inserted consisting of three glass spirals spaced about 4 cm. apart and to the top of which a light iron nail enclosed in a glass tube was sealed.

The liquids were stirred, at a constant temperature for about an hour by means of a magnetic stirrer. Around the neck of the tube as indicated in the diagram a solenoid (B) of bell wire was placed, connected in series with a bank of lamps. In parallel with the solenoid a circuit breaker (C) was connected to raise and lower the stirrer. The movement of the stirrer (E) was in this way made dependent on the periodic variation of the current in the solenoid and not in the actual making and breaking of the circuit.

It was found a four litre beaker (D) filled with water could satisfactorily control the temperature to one-tenth of a degree with the judicious use of a Bunsen flame and stirring the water continuously with air.

The experimental procedure was as follows: An aqueous solution was poured into the tube till its level was about that where the second capillary tube was sealed in. On top was placed an equal volume of ether which had been purified by washing, standing over calcium chloride and subsequent distillation, after sodium had been allowed to react for some two or three days. Rubber tubes fitted with glass plugs were placed over the ends of the capillary tubes and the glass stopper put in place. The mixture was stirred at a constant temperature when after an interval of one to one and one-half hours equilibrium was reached. Portions of each phase were then removed in the following manner. A hollow ground glass tube was inserted in place of the stopper after attaching a rubber tube to it. The liquid layers were then blown out through the capillary tubes into 25 c.c. specific gravity bottles, the first portions in each case being neglected. A definite volume of each layer was then titrated, or if one c.c. of the layer required too large a quantity of permanganate then one c.c. was diluted to 25 c.c. in a graduated flask and a definite volume of the dilute solution was titrated. In order to reduce errors to a minimum the same pipette was used for both layers.

In order to obtain concordant results one of the most important things noted was the efficiency of the stirring. A stirring stroke 5 cm. usually suffices but in any case the interfacial layer between the two phases must be continually broken. Probably the main reason for care in this direction lies in the fact that peroxide solutions, especially those of higher concentrations, are much heavier than ether. This precaution applies equally well when diluting a sample of the layer to a known volume. Vigorous stirring is necessary to ensure homogeneity.

The results obtained in the experiment are expressed in mol fractions of hydrogen peroxide per c.c. of the original water and ether layers obtained in the following way.

$$\text{Mol. fraction} - \frac{\text{no. of c.c. KMn04 per unit volume x K}}{\text{Mol wt. of H O}}$$

$$- \frac{\text{C.C. KMn04 per c.c. layer x .004287}}{34}$$

Temp. 25 C.

Mol.fraction Water	Ether	Grms. per c.c. Water layer	Partition Coefficient
.03544	.01890	1.205	1.87
.03227	.01563	1.097	2.06
.02952	.01314	1.0030	2.23
.02900	.01261	.9850	2.30
.02282	.008880	.7760	2.57
.01689	.005284	.5744	3.19
.01573	.004610	.5134	3.29
.01194	.002531	.4061	4.74
.009416	.001355	.3220	6.95
.009374	.001324	.3115	7.06
.005106	.0005873	.1697	10.95
.004709	.0004097	.1610	11.55
.004166	.0003530	.1415	11.82
.002838	.0002062	.09650	13.73
.001934	.0001252	.06578	15.42
.001231	.00007617	.04186	16.13
.0005090	.00003070	.01731	16.55
.0002571	.00001525	.00874	16.83

Temp. 0. C.

Mol. Fraction Water	Mol. Fraction Ether	Grms. per c.c. Aqueous layer.	Partition Coefficient.
.03740	.02418	1.2740	1.54
.02410	.01023	.2213	2.36
.01053	.002846	.3583	3.71
.005930	.0009394	.2016	6.31
.001442	.0001540	.04902	9.36

The Distribution of H_2O_2 between Water and Ether.

Discussion of Results.

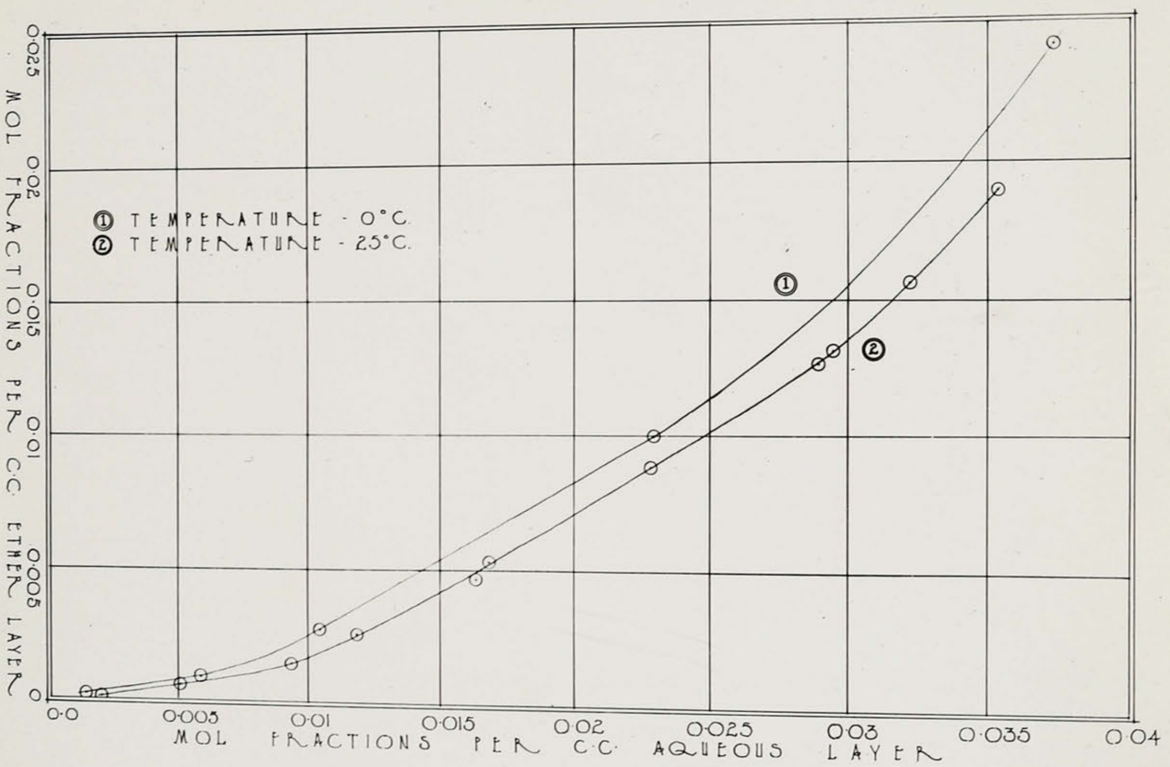
It is at once evident that the partition coefficients show no constancy in value. The first part of the curves 1, 2 and 3 drop quite sharply with a later tendency to become almost horizontal to the x axis at higher concentrations. It would appear had Kolossowsky worked through the whole range of concentrations his curve would have been between 1 and 3 for higher concentrations.

For very dilute solutions the curves 1, 2 and 3 all show a slight bend but without actually determining values for concentrations of the order of 1 and ,05 per cent we are not justified in assuming they become asyntotic to the x axis.

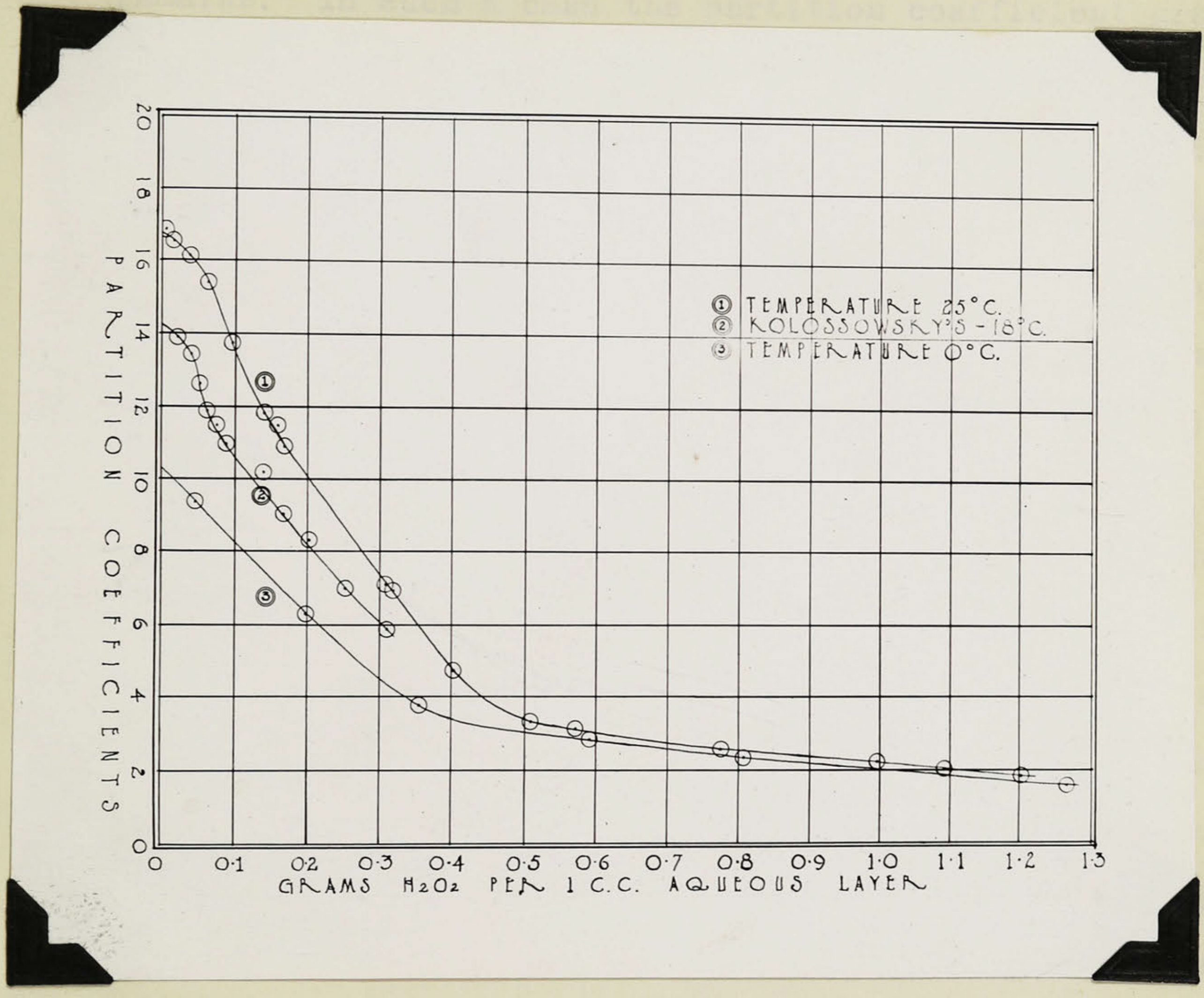
The question now arises as to the possibility of making quantitative predictions about such a system. Let us review the conditions essential for this purpose and see if the system approximates to them.

(a) Immiscibility.

If the distribution ratio is to be constant the phases must be mutually insoluble that the mutual solubility is not altered by the distribution of a third component. This condition is, of course, never completely realized. The distributed substance can, of course, do one of two things, it can either decrease or increase the solubility of the two phases.



CURVES OBTAINED FROM THE APPLICATION OF THE DISTRIBUTION LAW IN ITS SIMPLEST FORM



CURVES SHOWING THE RELATIONSHIP OBTAINED BY THE APPLICATION OF THE DISTRIBUTION LAW IN ITS SIMPLEST FORM.

If the former occurs then at high concentration, it may reduce it to a megligible amount. If the latter occurs the solubility of the two phases gradually increases to a point - consolute concentrations - that is only one phase remains. In such a case the partition coefficient gradually drops and ultimately becomes equal to unity. Considering the question from this point of view, only when the distributed substance is present in infinitely small amounts or is very dilute can we expect it not to affect the mutual solubility. The term dilute is a relative term because the lowering or increasing of the mutual solubility is a function of the properties of the components of the system. Therefore a given system may be investigated over a much wider range than any other without violating this condition.

Hydrogen peroxide appears to increase the mutual solubility of water and ether to a marked degree and some experiments were carried out on just this effect. If one adds alcohol to an ether-water solution one finds it requires five times as much alcohol as is required when a 52.5% peroxide solution is substituted for the water layer. This would indicate that the process of reaching consolute concentrations has been increased by the peroxide and that in this case the quantity of alcohol required to complete it, i.e. make the distribution unity is less than in the case where no third component is present. The system does not conform closely therefore to the principle of immiscibility.

(b) The State of aggregation of Hydrogen Peroxide in the two phases - Ether and Water.

The second condition required is that we assume either that the molecular condition is the same in both phases and that it can be represented by simple molecular or else that we know quantitatively what the molecular weight is and can calculate the constant of the homogeneous equilibria in each phase.

It has been definitely shown the law of partition in its simplest form is not applicable to the system. This may be due to one of two things, either the system does not conform closely enough to the principle of immiscibility or association occurs in one or both of the phases.

Evidence for association of Hydrogen Peroxide in the Ether Phase.

It is sufficient to say here that having measured the Dielectric Constant of pure Hydrogen Peroxide and its aqueous solutions we have found the values to be higher than water and for some of the solutions the difference is one of a different order of magnitude.

Association of a molecular species must be regarded as a type of chemical combination differing only from ordinary types of combinations in that it takes place between like rather than unlike molecules. It is evident that we must postulate some forces acting to bring about a more complex state. When a substance is known to possess a high dielectric constant we are justified in postulating a segregation of the electric charges of the molecule resulting in, or giving rise to, fields of force probably both electromagnetic and electrostatic in origin.

Let us dissolve this type of molecule in two types of solvent, viz. a polar and non-polar solvent, represented in this case by water and ether. One would expect the following conditions to result. In the former case two types of forces are active. Either the peroxide molecule will coalesce directly with the water molecule or it will tend to associate with itself. The problem then resolves itself into which of the two sets of forces will be most predominant. We are certainly unable to give a decisive answer but what we can say is that especially where water is present in excess solution for the most part ought to take place in the simple molecular condition.

In the latter case, viz. a non-polar solvent, the condition is not the same, here the forces acting between ether and peroxide are very weak and whenever molecules of peroxide collide the chances are fairly large they will tend to unite with themselves. In other words the conclusion is that peroxide molecules would tend to associate to quite a large extent in the ether phase. One knows neither the type of molecules in the ether phase nor the degree of dissociation at various concentrations of the molecular complex. It will be simply assumed the molecules are in the dimolecular condition and apply Nernst's equation. The equation to be used is $\frac{C_1}{\sqrt{C_2 (1-a)}} = K$ which was developed earlier.

Since we do not know 'a' the degree of dissociation of the complex molecules we will neglect it for the moment and calculate the ratio between the concentration in the water phase and the square root of the concentration in the ether phase. The following results were obtained.

Conc. of H O Water Phase / Conc. of H O Ether Phase.	Temp. 25°	Ratio

	Ratio.
$\frac{.03544}{\sqrt{.01890}}$	0.258
$\frac{0.03227}{\sqrt{.01563}}$	0.258
$\frac{0.02952}{\sqrt{.01314}}$	0.258
$\frac{0.02900}{\sqrt{.01261}}$	0.258
$\frac{0.02282}{\sqrt{.008880}}$	0.242
$\frac{0.01689}{\sqrt{.005294}}$	0.232
$\frac{0.01573}{\sqrt{.004610}}$	0.232
$\frac{0.01194}{\sqrt{.002531}}$	0.237
$\frac{0.009416}{\sqrt{.001355}}$	0.256
$\frac{0.009374}{\sqrt{.001324}}$	0.257
$\frac{0.005106}{\sqrt{.0005873}}$	0.237
$\frac{0.004709}{\sqrt{.0004097}}$	0.233
$\frac{0.004166}{\sqrt{.0003530}}$	0.222
$\frac{0.001934}{\sqrt{.0001252}}$	0.173

	Ratio.
$\frac{0.001231}{\sqrt{.00007617}}$	0.141
$\frac{0.0005090}{\sqrt{.00003070}}$	0.0730
$\frac{0.0002571}{\sqrt{.00001525}}$	0.0658

Conc. of H O Water Phase. / Conc. of H O Ether Phase.	Temp. C.	Ratio.
$\frac{0.03740}{\sqrt{.02418}}$		0.241
$\frac{0.02410}{\sqrt{.01023}}$		0.239
$\frac{0.01053}{\sqrt{.002846}}$		0.199
$\frac{0.005930}{\sqrt{.0009394}}$		0.180
$\frac{0.001442}{\sqrt{.0001540}}$		0.118

Curves were plotted and included below. Ratio as ordinates and concentration in water layer as abscissae, Both curves appear to become asyntotic to the concentration axis, but with a decided break in the curve both for the 25° and 0° curve. Let us neglect the breaks for the moment and consider if the curve is consistant in its general aspects.

In the first place the calculations used, assumed complete association of the peroxide molecul~~ar~~ over the whole range of concentrations. There is plenty of evidence to show that this is not to be expected for dilute solutions. Molecular weights in very dilute solutions substantiate this point of view. What the curves do allow us to presume is that if one properly allowed for the dissociation of the associated molecules for dilute solutions one would find the ratio approximately a constant.

We will now reconsider the Nernst equation $\frac{C_1}{\sqrt{C_2\,(1-a)}} = K$

For the most dilute solution under consideration at 25°C the ratio was found to be .0658, At this concentration let us assume $a = .9$. That is 90% of the molecules in the ether phase are non-associated at this concentration. We have found that $\frac{C_1}{\sqrt{C_2}} = 0.0658$ $\quad 1-a = .1 \quad \sqrt{1-a} = 0.316$

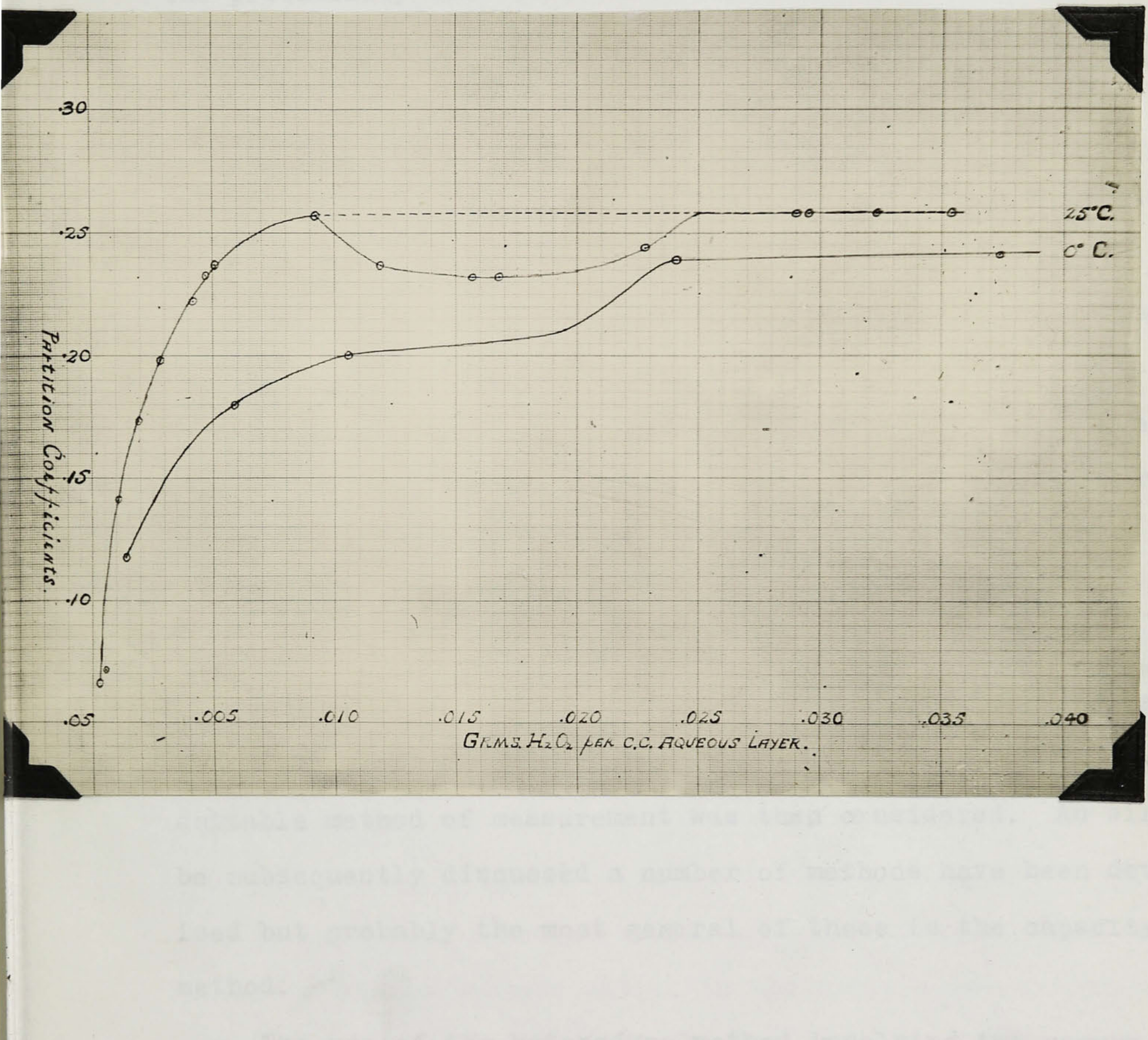
$$K = \frac{0.0658}{0.316} = 0.209$$

For the most concentrated solution at 25°C the ratio was .258. It is assumed here that $a = 0.1$ i.e. 90% are associated.

$1 - a = 0.9 \quad \sqrt{1-a} = 0.950 \quad K = \frac{0.258}{0.95} = .272$

If the values for a are reasonable then it is evident a fair constancy in ratio results from this calculation. We can offer no explanation for the derivation of the curve except that they are in the region where a compound between hydrogen peroxide and water is formed and also where a maximum value in the dielectric constant is encountered.

It, therefore, seems that the most important factor in the interpretation of the above system is the state of aggregation of the molecules in the two phases. On account also that a full consideration will be taken up in the next section of the thesis of association no further discussion at this point was deemed necessary.



By taking into consideration the state of aggregation of Hydrogen peroxide in the ether and water phases the above curves were obtained at 25 and 0°C

$$\text{The partition co-efficient} = \frac{\text{Conc in water phase}}{\text{Conc in ether phase.}}$$

Section -2-

THE DIELECTRIC CONSTANTS OF WATER, HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS.

General Introduction.

Sufficient physical chemistry data is available to indicate the probability that the dielectric constant of hydrogen peroxide is of the same order of magnitude as that of water.

Owing to the high value of water and its corresponding abnormalities, the determination of the constant for hydrogen peroxide and its solutions seemed to offer some interest. Irrespective, however, of the method employed it appeared necessary to have the peroxide come in contact with metal surfaces. Under these conditions decomposition and even explosion might result so that efforts were made to find a metal surface which would be inactive when in contact with either the solutions or the pure material, Ultimately it was decided that tin more nearly approached the ideal than any other metal which was tried.

The first difficulty of decomposition at metal surfaces having been for the most part eliminated, the choice of a suitable method of measurement was then considered. As will be subsequently discussed a number of methods have been devised but probably the most general of these is the capacity method.

The use of the heterodyne method involving two vacuum tube oscillators offered a convenient and accurate method for capacity comparison. The method is, as one might expect, comparatively new so that considerable amount of experimental work was necessary in order to use it for the measurements in question. A new type of cell was devised to serve the purpose which obviates the necessity of making lead corrections and sufficiently flexible to measure constants from 1 to 100. For the measurements of hydrogen peroxide and its aqueous solutions the cell was constructed entirely of tin.. Before going on to the experimental details and to illustrate the general significance of the dielectric constant in chemistry, an attempt will be made to give a fairly full account of the physical significance of the dielectric constant. As this is not measured directly but as a function of the capacity it is considered advisable to show clearly the relationship between the two quantities.

Following this the chemical significance of the dielectric constant is discussed from the point of view of polarity as evidenced by association, and indicated by types of valence forces, electro and co-valent, Finally the precise experimental method is developed, the results obtained are then given and it is ultimately shown how these specific constants illustrate the correctness of the general deductions.

At the end of the main section, using the values of refractive indices determined at three wave lengths for various strengths of solutions, the electrical moments of the peroxide and water molecules are given and the applicability of the Debye equation in the above cases discussed.

The Dielectric Constant.

The original conception of the dielectric constant began with Faraday and there is somewhat of a parallelism in the development of the idea and the atomic concept of electricity. Chemical combination is now considered to be either a shifting or a sharing of electrons or both and any physical constant capable of giving an idea as to the extent either of the above phenomena take place is significant in theoretical chemistry.

Unfortunately there are not a great many constants which give evidence as to the distribution of electricity in a molecule, so that at present the dielectric constant is considered one of the best guides in this respect. In chemistry one usually refers to the distribution of electrical charges in a molecule as "polarity" and subsequently an attempt will be made to develop the idea both from a qualitative and quantitative point of view. Before, however, this can be satisfactorily accomplished the physical significance of the dielectric constant must be dealt with briefly.

The Physical Significance of the Dielectric Constant.

The force of attraction between two oppositely charged bodies or the force of repulsion between two similarly charged bodies depends on two things, the degree of electrification of the two bodies and their distance apart. This relationship is expressed mathematically by $F \propto \frac{Q_1 Q_2}{R^2}$ where F represents the force between the two bodies q_1 q_2 the charges and R the distance in centimetres between them. Introduction of a constant in the equation gives $F = a \frac{q_1 q_2}{R^2}$ a - being a constant depending on the medium separating the two bodies. The reciprocal of a is known as the dielectric constant. In future it will be referred to as E. For the purpose of relative measurement air is taken as unity and all other substances are expressed relative to air. The general equation thus becomes $F = \frac{1}{E} \frac{qq_2}{R^2}$

Capacity and its relationship to E.

It is a well known fact in electrostatics that the potential produced inside a spherical conductor by a given charge varies with the size of the conductor. It can also be shown experimentally that if the same charge be given to two conductors differing in size different potentials result. These facts are expressed by saying that different conductors have different capacities. The quantity of electricity Q given to a conductor is proportioned to the potential V u $Q \propto V$ or $Q = C V$, that is the ratio of the quantity of electricity to the potential is a constant for a conductor of any given dimensions. The constant C is called the capacity of the conductor.

In order to measure a capacity a condenser is used. Its principle is best understood from the following considerations suppose a metal plate be charged to a positive potential V. If another insulated plate be brought into the immediate vicinity of the charged one inductive displacement takes place, i.e. the side of the insulated plate next to the charge one assumes a negative charge and the other side a positive charge. The effect on these induced charges act in the following way on the charged plate. The induced negative reduces the charge on the charged plate, the positive increases it. The positive, however, is further away than the negative i.e. (the thickness of the plate). The ultimate effect, therefore, is to slightly reduce the potential of the charged conductor. If the insulated plate now be grounded the positive potential is removed and the effect is to considerably weaken the potential. Using the formula $\frac{Q}{V} = C$ it is evident as V decreases C increases. It is evident then that the capacity of a charged plate is increased by bringing a grounded plate in close proximity. Such a system is known as a condenser.

Assume that a condenser has a capacity of C units in air. If it is immersed in a medium of dielectric E the potential will be $\frac{1}{E}$ of what is in air, that is the capacity becomes E times what is was before. The actual mathematical relationship for the connection between capacity and dielectric constant can be obtained for the simple case of a two plate condenser in the following way. Imagine a closed cylindrical surface the ends of which lie on opposite sides of a charged plane. It can be shown that at any point infinitely close to the charged plane the force in the surface equals P, where P - surface density. If the value of the dielectric constant is E $F = \frac{2\pi P}{E}$

If two parallel plates A sq.cm. in area d.cm. apart have a surface density charge P on one plate - P is induced on the other. A positive unit will be repelled by one plate by a force $\frac{2\pi P}{E}$ and attracted to the other by $\frac{2\pi P}{E}$ The total force acting then becomes $\frac{4\pi P}{E}$. The work done in carrying the charge from the positive to the negative plate = F x distance - $\frac{4\pi P}{E} \times d$ = potential by definition. Now C =

$$\frac{Q}{V} = \frac{AQ}{\frac{4\pi Pd}{E}} = \frac{EA}{4\pi d} \qquad \text{For air } C = \frac{A}{4\pi d} \qquad E = 1$$

$$\text{For medium } C = \frac{EA}{4\pi d}$$

$\therefore \frac{C \text{ medium}}{C \text{ air}} = E$ i. e. the ratio of the capacity of a condenser under the two outlined conditions gives the dielectric constant of the medium.

A brief discussion has been given of the relationship between capacity and dielectric constant. The Kinetic interpretation of the latter will now be discussed.

The Kinetic Interpretation of the Dielectric Constant.

This interpretation so beautifully worked out by Debye gives us both a mental picture and a mathematical idea of polarity, in terms of the dielectric constant. In order to appreciate how this is accomplished both the qualitative and quantitative aspect of the problem will be considered.

(a) The Qualitative aspect of the problem.

This is best understood by developing ideas concerning the refractive index of a substance. In 1858-63 Gladstone and Dale and Landolt showed that $\frac{N-1}{d}$ - constant which was characteristic of a substance N = refractive index and d = density of the substance. It was found however that the constant varied with the state of aggregation and was not applicable to mixtures. In 1880 Lorenz in Copenhagen and Lorentz in Dryden deduced on a sound theoretical basis the well known Lorenz-Lorentz equation. i.e. $\frac{N^2-1}{N^2+2} \frac{M}{d}$ - (Specific refraction (of a substance.

In order to fully appreciate the application of this equation the relationship of the dielectric constant to polarity it is necessary to show how the Lorenz-Lorentz equation was obtained

To do this the assumption is made that the molecules are spherical, electrical conductors. If these molecules are placed in an electric field the centres of gravity of positive and negative electricity (present in equal amounts) will be shifted from the centre of the sphere and result in induced electrical dipoles. Such dipoles will act to reduce the charge on the bodies producing the field and in this way we can account for the dielectric constant. The definition of the dielectric constant of a molecule is the extent to which a molecule due to its induced dipoles diminishes the force between the charged bodies producing the field, relative to air taken as unity.

Clausius developed a relationship between the fraction of the volume of a substance occupied by the molecules to the dielectric constant. He found that $E = \frac{1+2u}{1-u}$ where E = dielectric constant and u = volume of molecules. A simple algebraic transposition of the previous equation gives where a gram molecule M and density d is under consideration ,

$\frac{E-1}{E+2}\frac{M}{d}$ This quantity is called P_o and represents the polarisability of the molecule.

In Clerk Maxwell's electromagnetic theory of light it has been shown that for infinitely long waves the square of the refractive index is equivalent to the dielectric constant. Therefore if we substitute N^2 for E in the Clausius equation we have $\frac{N^2-1}{N^2+2}\frac{M}{d} = P_o$ This is the Lorenz-Lorentz equation previously referred to. For purposes of comparison the two equations may be written down.

(1) $\frac{E-1}{E+2}\frac{M}{d} = P_o$ (2) $\frac{N^2-1}{N^2+2}\frac{M}{d} = P_o$

Mathematically the two equations must be identical if $N^2 = E$ but strange enough although (2) is valid for all substances (1) is not. At first the reason was assumed to be that the Maxwellian relationship was in error, a supposition, however, that proved to be incorrect. The reason for the inapplicability of equation (1) was left to the genius of Debye. /3

To understand Debye's reasoning one must reconsider the Clausius equation. As stated before there is a quantity U representing the actual space occupied by a molecule. The equation of Van der Waal's contains a quantity b also related to the volume of the molecules, b from critical data $= \frac{Vc}{3}$. Vc represents the critical volume. b is also four times the actual volume of the molecules $= 4P_0$ ∴ $P_0 = \frac{Vc}{12}$. It is also known that $\frac{Pc\ Vc}{R\ Tc} = \frac{3}{8}$ ∴ $P_0 = \frac{1}{32}\frac{R\ Tc}{pc}$ where R is the gas constant Tc = the critical temperature and pc the critical pressure.

Evidently two methods are available to calculate the polarisability of a molecule i.e. critical data and dielectric constant data.

Debye then calculated the values of the polarisability from the two sets of data. He computed P for O_2 H_2 and NH_3. by the two methods. They gave the following result:

Gas	P_0 from E	P_0 from critical data
H_2	2.04	4.98
O_2 Two values given to show	4.05	6.20
O_2 error in results.	4.05	7.83
NH_3	63.0	9.52

One thing is to be noted, that although values of P agree for Hydrogen and Oxygen the order of magnitude is different for Ammonia. Why?

The polarisability of a compound ought to be the sum of the values of the constituent atoms. P for ammonia as calculated from its constituent atoms equals 5.22 CM^3 while for the compound itself it comes out to be 63.0 CM^3. Finally P_0 ought to be independent of the temperature. We find, that for ammonia it changes according to the following figures:

Temperature	P
292.2	57.57
309.0	55.01

Temperature	P_o
333.0	51.22
387.0	44.99
413.0	42.51
446.0	39.59
448.0	39.50

Debye had the following facts at his disposal:

(1) For some substances P_o calculated from dielectric constant data was much larger than from critical data.

(2) The additive P_o as calculated from the constituent atoms was much smaller than for the compound itself composed of the atom.

(3) In some cases the P_o was considerably cmaller at higher temperatures.

What conception would account for these facts? Debye came to the conclusion that the only theory consistent with these facts was to assume that in those molecules which showed the above abnormal properties permanent dipoles exist, i.e. - under ordinary conditions some molecules have their electrical charges segregated. It will now be considered how this conception agrees with observed facts.

(1) In the Clausius equation the assumption was made that any polarity possessed by a molecule was an induced one. If, however, the molecule already possesses a dipole apart from the induced one, then the dielectric constant as measured will be equivalent to the induced dipole plus the permanent. P_o as calculated will be too large.

(2) Any constituent atom may have no permanent moment but the combination of such atoms may lead to one. This will lead to the expression sum of induced polarisability of atoms equal polarisability of molecule plus permanent polarisability.

(3) The molecules will act like little magnets and will on the average orientate themselves in a definite fashion. Increase in temperature will increase the random motions of the molecules and the probability of the dipoles occupying a mean position in preference to any other becomes less as the number of collisions increase. The effect they exert will therefore decrease with rise in temperature.

One other question might be taken up in this connection, why, for most substances, are the values of P_o calculated from refractive index measurements nicely additive? It must be remembered that these measurements are made at extremely high frequences viz - that of light. Under these conditions the permanent moment does not get an opportunity to orientate itself the way it does when dielectric constant measurements are made. This is due to the fact that the oscillations pass through the liquid in question so rapidly that the dipoles are unaffected.

Quantitative Considerations of the Polarity of a Molecule and its Dielectric Constant.

Let a free space be considered under the influence of an electric field H. Upon placing matter in this field it assumes some new value D. The increased number of lines of force resulting from the action of the matter placed in the field may be considered as coming from the two ends of the volume. Each unit volume then contributes $\pm\ 4\pi P$ new lines of force $\therefore$ $D = H \pm 4\pi P$ for any one molecule. This consideration really applies to continuous medium. Each molecule however being surrounded by many others is influenced by its neighbours. When, therefore, the influence of the outer field is considered on any particular molecule the effect of the surrounding ones must be taken into consideration. This effect has been called by Debye the inner field and is denoted by F. $F = H + \frac{4\pi P}{3}$ where the fraction $\frac{1}{3}$ may be considered as the effect along one axis. The average moment of a molecule is given as $\overline{m} = bF$.

If there are Z molecules in unit mass and the density is d then $P = Zd\,m = ZdbF$.

As $F = H + \frac{4\pi}{3}P \quad \therefore \quad P = Zdb(\frac{H}{3}4\pi P)$ or $P = \frac{Zdb}{1-\frac{4\pi}{3}Zdb}H$

Now $P = KH$ where K = electric susceptibility of the molecule.

$\therefore \quad K = \frac{Zdb}{1-\frac{4\pi}{3}Zdb}$ Also by definition $D = EH$ where E = dielectric constant. $\therefore \quad E = 1 + 4\pi K$ - since $D = E(1+4\pi K)$.

$\therefore$ algebraically $\frac{E-1}{E-\frac{\frac{4\pi}{3}-4\pi}{\frac{4\pi}{3}}} = \frac{4\pi}{3}dzb$

or $\frac{E-1}{E+2} = \frac{4\pi}{3}dzb$

If b the polarisability is a constant, then $\frac{E-1}{E+2} \times \frac{1}{d}$ a constant. If, however, the value varies with temperature then it has to be assumed the polarisability varies i.e. it is a function of the temperature and led Debye to assume molecular dipoles. To obtain the Lorenz-Lorentz equation put $N^2 = E$ then $\frac{M}{d}\frac{N^2-1}{N^2+2} = \frac{4}{3}\pi b\,NA$ i.e. NA = avogadro's Number = Mz

It has been mentioned that P in certain cases varies with the temperature. Debye, therefore, attempted to find the cause of the variation of "b". If it be assumed that the dielectric constant has another origin besides the induced dipoles the problem appeared capable of solution. Two types of action were then assumed. There is the usual separation of charges expressed quantitatively in the Clausius -Mosotti Law.

In some molecules fixed dipoles also exist which tend to set themselves parallel to the field. This orientation is to some extent destroyed by thermal agitation but for any temperature they will on the average assume some definite position. Their effectiveness however will continually decrease with rise in temperature. Since the magnitude of the dielectric constant is a function of the orientation of the dipoles it also will show a decrease with temperature.

To compute the temperature effect all that is required is to assume the molecules possess a fixed moment μ. The classical kinetic theory allows us to assume that the potential energy of these dipoles will be in equilibrium with the kinetic energy of the molecules. For a field F and electrical moment m. $m F =$ Potential energy $= u F \cos\theta$ where θ is the angle between m and F for any given temperature. Therefore $- m F = - u F \cos\theta$. The moments for all the different angles θ can assume can be averaged according to their probability of appearance. It is found on this basis that $\frac{\bar{m}}{u} = \frac{\mu F}{3KT}$ where K is 1.37×10^{-16}
T is the absolute temperature.

or $\frac{\bar{m}}{F} = \frac{\mu^2}{3KT}$ for a single molecule.

For those molecules where $\mu > 0$, $\frac{\mu^2}{3KT}$ must be added to the polarisability as obtained from the Clausius Mosotti Law. The final equation then becomes

$P_o = \frac{4\pi}{3} N_A \left(b + \frac{\mu^2}{3KT}\right)$ Where P_o is measured from refractive index data $\mu = 0$.

Experimental Verification of the Theory.

$$P_o = \frac{4\pi}{3} Na \left(b + \frac{1}{3} \frac{\mu^2}{3KT}\right)$$

$$\text{Let } C = \frac{4}{3}\pi NAb$$

$$\text{Let } a = \frac{4\pi}{9} NA \frac{\mu^2}{KT}$$

Then $P_o T = a + c T = \frac{E-1}{E+2} \frac{M}{d} T.$

Plotting $P_o T$ against T a straight line should be obtained. An example of the use of this equation in calculating μ for water will be dealt with later.

Association. 14

In the widest sense of the term, association embraces the whole of the phenomena of chemistry and physics. The smallest chemical unit is made up, according to our modern views, of association of electrons the number and arrangement of which give specific properties to any given atomic species.

The molecule of an elementary substance may vary in complexity from the simplest possible character like that of the rare gases to that of great complexity as we find in sulphur. Molecules of compounds likewise are associated which may be split up into simple molecules under the action of certain forces such as heat, electrical stress and solvent action.

Instances of molecular association were observed quite early in the development of modern atomic and molecular theories. The vapour density determinations of Dumas and Mitscherlich coupled with Cannizarro's interpretation eventually proved that many gaseous molecules were not elementary; while later work was proceeding on gases Raoult was concerned with solutions investigating the relationship of molecular weight to the lowering of freezing point and vapour pressure. This led eventually to the extension of the simple gas laws to dilute solution by Van't Hoff. Anomalies were soon observed for two distinct classes of substances viz. those that lowered the freezing point to a greater extent than the calculated value and those that did the reverse. If the former case be due to dissociation the latter must be considered as resulting from association.

Molecular Complexity in the Liquid State & Physical Properties

The determination of the molecular state of matter other than the highly diluted, is attended by many difficulties. Although in theory Avogadro's hypothesis can be applied to gases and very dilute solutions, all methods available for the liquid state must be classed as empirical. All one is capable of doing at the present time is to institute a comparison of the molecular properties of different liquids. Generally it is found that the molecular property of a liquid is additive, i.e. depends on the nature of the substance.

A large number of equations have been used connecting the molecular weight of a substance with some specific physical property of a liquid. As an example, take Trouton's rule $Ml = Kt$ where M = Molecular weight, l = heat of vaporization T = absolute temperature and K a constant. As a result of the application of this simple rule leading to many exceptions we divide liquids into two general classes - viz. normal and associated liquids.

Evidence is also obtained from (a) vapour pressure data (b) boiling point data (c) critical data (d) dielectric constant.

(a) Usually a substance non-associated is very volatile. The effect of molecular association is made evident from Van der Waal's equation, viz $\log p - \log p_c = k \frac{T_c - T}{T}$ where T_c and p_c represent critical temperature and pressure and T the temperature at which p is required. In such a case k is not a constant for a large number of liquids usually exceeding a value 3.06.

(b) If the vapour pressure is diminished by an increased state of aggregation of the molecule obviously the boiling point is raised. Actually it has been demonstrated that the mass of the molecule is at least qualitatively related to its boiling point.

(c) The determination of the value of the critical co-efficient is a criterion of the condition of a molecular species. Already it has been mentioned that $\frac{pc\ Vc}{R\ Tc} = 3/8$ and also that the molecular refraction MR equals $\frac{Vc}{12}$

Therefore $\frac{pc\ 12\ MR}{R\ Tc}$ equals 3/8

or $\frac{Tc}{pc}$ equals $\frac{1}{k}$ MR.

A number of normal substances have a value of $k =$ 1.8 others about 1.1. This method though valuable is ~~mixx~~ limited to the ease with which critical data can be obtained for a given substance.

The simplest method probably known for determining in an approximately quantitative way the state of aggregation of a substance comes from the Ramsay and Shield's constant. This method stated briefly depends on the measurement of the temperature coefficient of surface energy.

$$\frac{d\left(\lambda\left(\frac{M}{d}\right)^{2/3}\right)}{dt} = \text{Constant}$$

M being the molecular weight λ the surface tension and D the density. The assumption is made that the molecules in the surface of the liquid are representative of the whole body of the liquid. This assumption sometimes leads to absurd results. Rather it would be correct to say that this constant allows one to classify liquids under two general headings, normal and abnormal.

Degree of Association and Dielectric Constant of a liquid -- Polarity.

From the physical properties already discussed it is evident that there is justification in considering liquids to belong to one of two classes, i.e., normal or abnormal. The justification however lies only in experimental facts, but no reason for such behaviour is to be found in the constants already considered. The purpose of this section is to attempt to show why one should expect to find these two types of liquids.

To do this it seems in place to briefly review the meaning of the dielectric constant so far as its significance in physical chemistry is concerned. Briefly then the capacity of a dielectric liquid depends on the type of molecule with which one is dealing. If the electrical charges in the molecule are permanently segregated a polar molecule results. The rotation or extension and orientation in the presence of a field increases the capacity of the condenser so that polarity and dielectric constant are for purposes of chemistry closely related terms, i.e. the magnitude of the dielectric constant indicates the moment of the polar groups and the moment in turn on the charge and distance between the dipoles of the liquid.

Now just as with the other physical properties, two classes of liquids appear to exist, i.e., those possessing low dielectric constants on the one hand and high on the other. Instead of calling these liquids normal and abnormal, they are called non-polar and polar because as indicated above the higher the dielectric constant the more polar is the molecule. It can be shown that a relationship is to be expected between the state of aggregation of a substance and its electrical properties.

On the whole, substances which have been found to be strongly associated usually have high dielectric constants. It must be remembered however the converse of the above proposition is not necessarily true. In the absence of a very reliable method for determining the degree of association of any liquid, the Ramsay and Shields constant has been employed. A number of compounds, association factor and dielectric constant are listed below.

Substance	Association Factor	Dielectric Constant
Formamide	6.2	84
Water	3.8	84.4
Formic Acid	3.6	58.0
Ethyl Alcohol	2.7	26.
Acetone	1.3	21.2
Carbon Tetrachloride	1.0	2. 25
Benzene	1.0	2.3
Ether	1.0	4.3
Nitrobenzene	1.0	35.5

The only outstanding exception in the above table is that of nitrobenzene. It association factor is unity and yet it possesses a high dielectric constant.

Generally however, the above table serves to indicate a connection between the magnitude of the dielectric constant and association.

It is reasonable to conclude that polar molecules having strong fields of force unite to form larger aggregates by ~~mx~~ neutralizing those of a like molecular species.

A high dielectric constant is evidence that the fields of force around a molecule are large and tend to give rise to association.

The molecular condition of a liquid dissolved in polar and non-polar solvent.

If a polar liquid is dissolved in a non-polar one, the polar liquid will tend to unite with itself in preference to the non-polar solvent. One may expect it to be associated. If the same liquid is dissolved in a polar solvent, the chances of the solute remaining in a simple molecular condition are large, because three forces almost equal are at work, i.e., those between the solvent,-solvent, solvent-solute, and solute-solute and the predominance of any one is limited, depending on the specific characters of the components. As mentioned in section I of this thesis, these considerations appeared to be satisfactory to explain the system hydrogen peroxide, ether, water.

In summing up, the conception of association a combination of like molecular species is an electrical property of the molecule due to segregated electrical charges which in turn give rise to fields of force predominant in determining the combining power of the molecule with itself.

Polarity and Chemical Nature 15.

In the preceding section the relationship between polarity and some physical constants has been discussed with special reference to the dielectric constant. In this case it will be shown what types of molecules from a purely chemical point of view exhibit polarity.

(a) The polarity of groups or radicles

In many cases the introduction of a certain type of group to a molecule introduces decided polarity to the molecule as a whole. A hydroxyl group attached to alkyl residues, giving rise to alcohol, is an excellent example. It is found that the size of the relatively non-polar alkyl residue decreases the magnitude of the dielectric constant on passing from the lower to the higher alcohols. Thus methyl, ethyl, propyl and amyl alcohols have dielectric constants 32, 25, 22, and 16 respectively, which means as the size of the alkyl residue increases less leverage is exerted to orientate the molecule in a definite direction in preference to any other.

(b) The Symmetry of the molecule

Usually the nitro group is polar as in nitromethane and nitro-benzene, but in tetranitromethane such is not the case, the dielectric constant being 2.1 as compared to 40 for nitromethane and 36 for nitro-benzene.

In the case therefore of tetranitromethane the polar groups evidently balance each other due to a symmetrical arrangement of the groups.

Again halogen derivatives of benzene can be taken as examples, i.e., Chloro, bromo, and iodo-benzene. In passing from chlorine to iodine, the electro positive character of the elements increase and it is found that the dielectric constants of the three compounds are 11, 5.2 and 4.6. The introduction of an electropositive element would appear to decrease the dielectric constant. The same is true in many instances.

(c) Catalysis, Orientation, and addition Compounds.

Although Baker's work on intensive drying is in some cases open to criticism, yet it is generally conceded that small traces of water vapour do profoundly affect the velocity of a chemical reaction. For this purpose it may be assumed that the velocity of a reaction is dependent on three things, the number of collisions, the intensity of the impact and time the molecules remain in contact after collision. It appears likely the last condition is linked up with the influence of the catalyst, because the few fields of force surrounding the water molecule will be able to hold the colliding molecules long enough together to cause a union to take place, i.e., the water prevents an approximation to a perfectly elastic collision between the reacting molecules. This idea is further substantiated by the large number of hydrates known to be formed and that in general strongly additive properties are linked up with high polarity.

It is not the intention to deal fully with the phenomenon of orientation in liquid surfaces, or liquid crystals. All that is necessary to remark here, is that the only logical explanation of the phenomenon seems to be that where the proper physical and chemical conditions exist the electrical and magnetic properties of molecules make themselves evident.

The modern concept of Valence and polarity 16

Debye's theory of dielectric constants already discussed makes it evident that molecules possessing permanent dipoles ought to exist. Dielectric constant determinations have confirmed this point of view and the other physical properties briefly reviewed, show that polar and non-polar was a logical classification. From a historical point of view the problem is similar to the application of the dualistic theory of Berzelius to the substitution of chlorine into acetic acid.

Two types of linkages are evidently required, one ionizable and due to electrostatic attraction, the other non-ionizable. This non-ionizable linkage may take one of two forms so that actually for convenience, three types of linkage are recognized.

In general then chemical evidence points to three types of linkage of atoms in a molecule.

(1) Polar linkages of Kossel.

(2) Non-polar linkages of Lewis.

(3) Co-ordinate linkages of Werner.

Kossel pointed out that any element immediately preceding an inert gas is strongly electronegative and one following strongly electropositive. We can interpret this to mean that electronegative elements tend to take up electrons and electropositive to give up electrons in their striving to obtain stable configuration of a rare gas. A linkage then between strongly electropositive and electronegative elements results in a shift of electrons so that as a result the electrical charges are so to speak segregated. The extent of this segregation is indicated by the dielectric constant. A liquid then possessing at least one electro-valence will show polarity.

Kossel's point of view is hard to realize in the case of like atoms forming molecules. Thus most gases form under ordinary conditions atomic complexes called molecules. The dielectric constants of many of these gases is very small and further we should not expect two like atoms to give and take electrons. Lewis made the suggestion the molecule is due not to shifting but rather to a simple sharing of the electrons each atom making use of the other to form a configuration similar to that of a rare gas. The type of molecule so obtained will be non-polar.

There is however a second aspect to the idea of sharing. Normally each atom concerned shares with its neighbour, as described above. This sharing can also be considered due to one of the atoms sharing both with its neighbour. This is called co-ordinate co-valency.

Due to the position of carbon in the periodic table it has neither pronounced electropositive or electronegative characteristics, i.e., it as readily gives as takes electrons. As a result carbon exhibits either electro valence or co-valence or both in a given compound. If all the groups are attached by sharing as in simple hydrocarbon chains then the polarity of such a compound may be negligible. The paraffins are an example. If on the other hand one group is introduced such as OH, NO_2 etc., then this group may be assumed to result in an actual shift (in many cases) of an electron and the degree of this shift is qualitatively measured by the dielectric constant. This view is substantiated in the case of either Alkyl or aryl - monohalogen derivatives when the halogen ability to take up electrons decreases as we pass from the chlorine to iodine as previously mentioned.

A polar molecule nay now be described as follows:

(1) The polarizability of its constituent atoms is not additive.

(2) The dielectric constant decreases with the temperature.

(3) At least one group must have an electrovalence linkage.

(4) It leads to a complex state of aggregation.

Experimental Method for the Measurement of Dielectric Constants.

Historical.

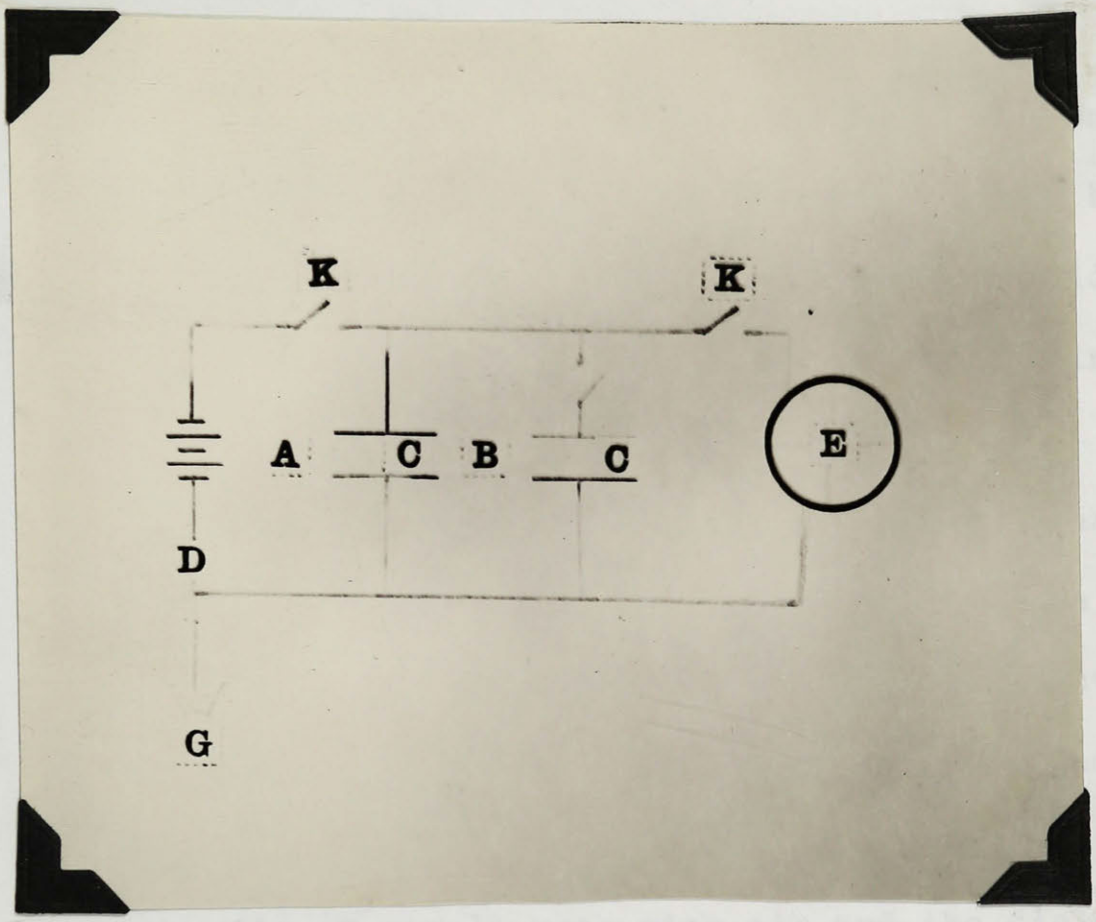
Probably the earliest method of investigation was that employed by Faraday. He used two condensers of equal dimensions. In one the medium was air and in the other the substance whose dielectric constant was to be measured. The diagram and a brief explanation will make the method clear.

A and B are two condensers of capacities. C_1 and C_2: D is a convenient battery, K a quadrant electrometer, M_1 M_2 M_3 are keys. It will be noted one pair of quadrants, one terminal of the battery and one plate of each condenser are earthed at G. If Q denote the charge on A alone $Q = C_1 . V_1 .$ in the second case $Q = (C_1 \text{ plus } C_2)\ V_2$

If d_1 and d_2 are the electrometer deflections then $\frac{C_1}{C_2} = \frac{d_2}{d_1 - d_2}$

This ratio will measure the dielectric of the substance.

In dealing with liquids Hopkinson used a sliding cylindrical condenser whose capacity for various settings was accurately known. Instead of using two condensers and different deflections, the condenser was adjusted for air, then the liquid introduced and value of the capacity altered



Quadrant Electrometer Method for measurement of dielectric constants.

A and B are two condensers of capacities C_1 and $C2$ K_1 and K_2 are switches. D is a battery. E Electrometer. G the earth connection.

to give the same deflection as previously. The ratio of the capacities for the same deflection gave E.

Silow's method[17] consisted in keeping the potentials constant and measuring the actual force in **dynes** between two **conductors** first in air and then in the liquid in question. A quadrant electrometer was used as in the above to measure potential.

Arons and Cohn[17] modified Silow's method by substituting an altertaning current for the direct. They were able to measure any liquid including water quite satisfactorily.

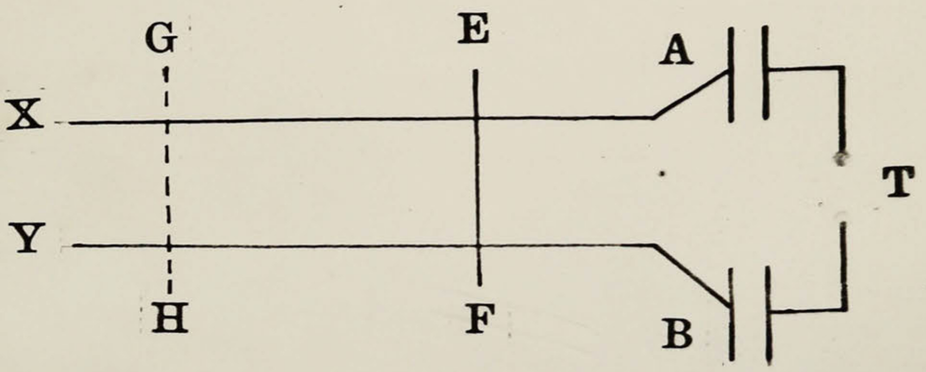
Among the more modern methods may be included that of **Nernst**[18] which represents the best known capacity method. The capacity of a cell both with air and the dielectric is balanced in one arm of a Wheatstone bridge, against a known capacity in the other arm. The source of electrical energy is an oscillator very similar to that used in conductivity methods. In order to obviate errors due to slight conductance of the medium the standard condenser is shunted by a variable resistance whose value is made the same as the liquid. The cell used is of a simple two plate variety and usually standardized by some substance whose value is accurately known.

Drude's[19] method has been extensively used and merits consideration. Use is made of standing waves from a **Tesla** coil in a pair of parallel conductors. The included diagram will help to make the idea more intelligible. Suppose the wire bridges E F to be a **node** and second wire bridge G H to be moved along the wires until it occupies the position of the next **node** . A **Geissler** tube conveniently connected will indicate the position. The distance between the two bridges is one half wave-length so that the wave length in air is found. If a liquid now surrounds the wires, the wave length can also be determined. The refractive index N equals $\frac{W_1}{W_2}$ where W_1 and W_2 are the wave lengths in air and the liquid . since N^2 equals E E equals $\frac{(W_1)^2}{(W_2)^2}$

The resonance method for the measurement of Capacity.

This represents another **example** of the use of the capacity method. If one has a means of comparing the capacity of a condenser having some substance between its plates with its capacity when air is used as a dielectric, the constant can readily be calculated.

The method of measurement is best understood through the following **consideration and diagram.** If the **condenser** AB charged to a potential by means of a battery is allowed to discharge through a coil L

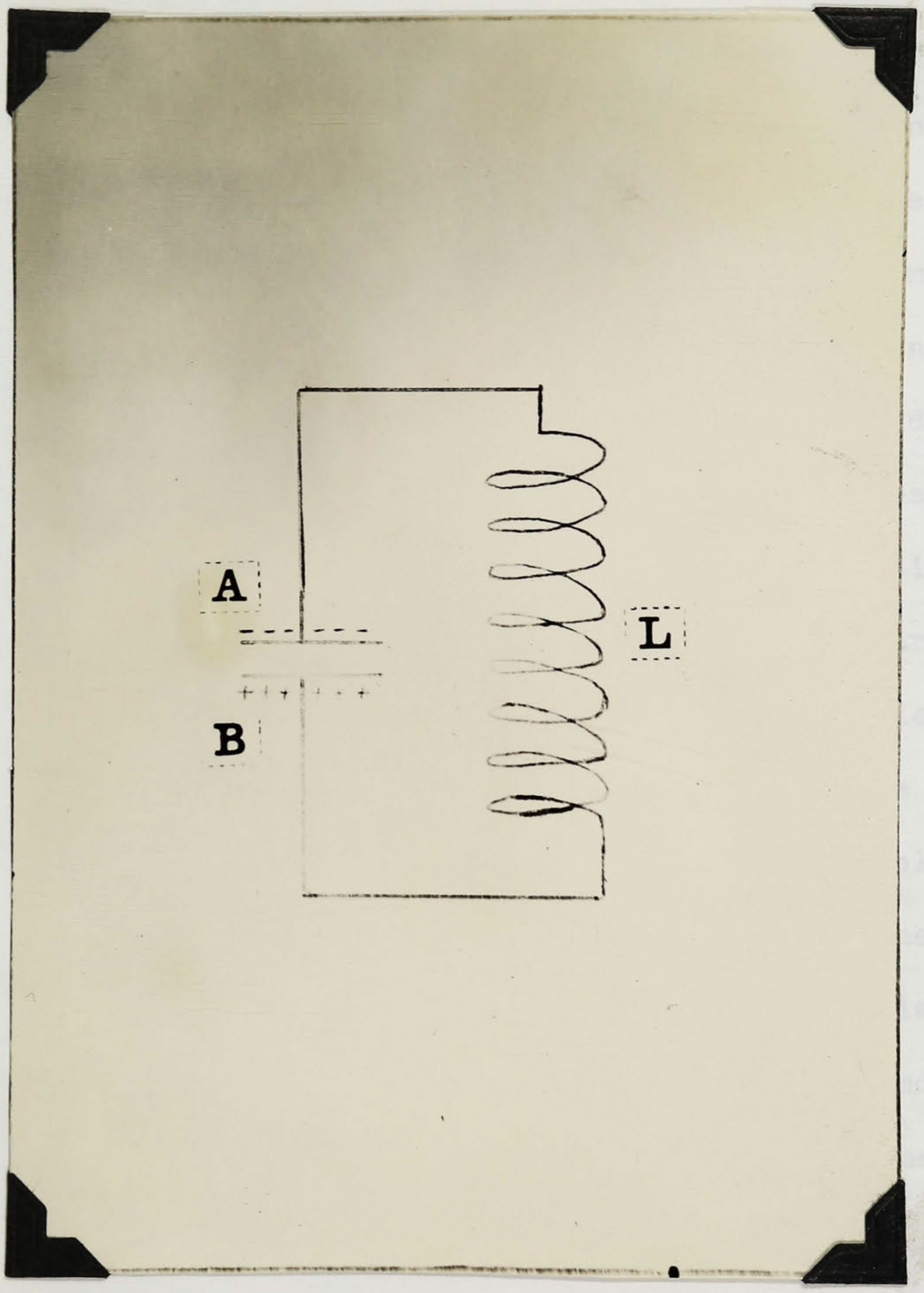


Drude's Method for determining dielectric constants.

T represents a Tesla coil

A & B metal plates

X	Y	parallel conductors
E	F	position of first node
G	H	position of second node



Diagrammatic representation of an oscillator

A and B are two plates of a condenser
L is an inductance.

electrons from the negatively charged plate A flow through the coil L to the plate B. The current of electrons does not stop flowing when A and B have reached the condition of equal potential, for when the stream of electrons begins to slow up as a result of falling potential difference between A and B the electromagnetic field generated in L tends to keep it in motion, and as a consequence plate A continues to lose electrons and becomes positively charged and B assumes a negative one. Discharge then occurs in the opposite direction so that the electrons swing back and forth through the circuit from plate to plate very much like a moving pendulum, until the electrical energy is dissipated as heat in overcoming the resistance in the circuit. The frequency of this oscillation depends upon the capacity of the condenser and the inductance or number of turns on the coil L as shown by the equation.

$$n = \frac{1}{2\pi} \sqrt{L \times C}.$$

n = frequency. L = Inductance C = Capacity.
This equation is valid if the resistance of the circuit is small.

In the resonance method a vacuum tube supplies the energy to keep the circuit continually producing electromagnetic waves of a frequency depending on the above named factors.

Obviously if one of the factors governing the period of oscillation be fixed then N will be directly proportional to the variable one. In this case the Inductance has a fixed value and any change in frequency is determined by the capacity in the circuit.

Suppose now two such oscillations as described above with the same inductances produce simultaneously electromagnetic waves. If the capacity in one be C_1 the other C_2, then N_1 equals $\frac{K}{C_1}$

N_2 equals $\frac{K}{C_2}$

If N differs from N_2 by a small amount, C_1 and C_2 also differ to the same degree, and ultimately if C_1 and C_2 are made equal N_1 and N_2 are equal.

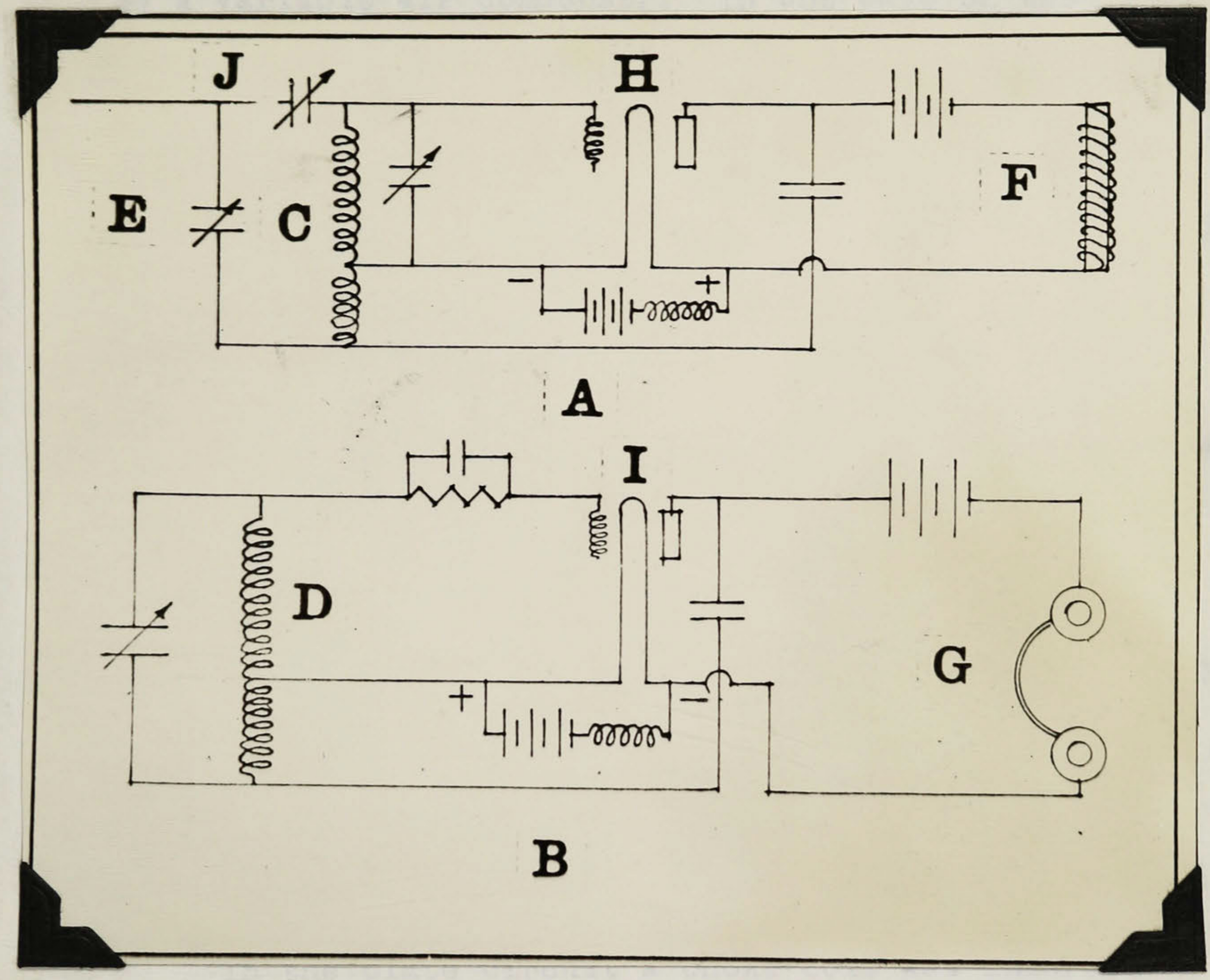
For purposes of explanation as to what happens under these conditions an analogy in acoustics may be used. Take two tuning forks which will vibrate at 256 per second and load one of them with a small amount of sealing wax, thereby altering slightly the frequency of one from its normal value. Upon setting these two forks vibrating, beats are heard and the number per second indicates how much difference in frequency exists between the two.

If N_1 differs from N_2 by a small amount, the two electromagnetic waves will also produce beats, but they of course have to be detected by a pair of telephones. An approximation to complete resonance results when the frequency of the beats is too low to be heard. If instead of using even a variable condenser in one oscillator, both the inductance and capacity be fixed, then the relative capacity at the null point in the other oscillator can be accurately determined.

The apparatus used can be considered as made up of a fixed oscillator or receiver and a variable oscillator

In the circuit of the latter, in **parallel** with a tuning condenser a cell is connected for the determination of the dielectric constants of various liquids. In use the variable oscillator is brought to resonance - the capacity reading is C, the cell is connected, the capacity reading is C2 for resonance. Therefore $C_1 - C_2$ equals capacity of the cell. Having given a general survey, the details of the oscillators and the method of measurement will be dealt with.

Two Hartley oscillators were employed because of the steadiness of operation and simplicity of construction. A wiring diagram of the oscillators is included. The inductances consisted of 75 turn honeycomb coils. A tap taken off at 50 turns was connected to the filament lead. Each of these inductances were shunted



Wiring diagram of oscillators used in resonance method for dielectric constant measurements.

A. Variable oscillator
  J. Series condenser to reduce effects of conductivity
  E. Tuning condenser
  C. Honey Comb coil
  H. Vacuum Tube - Radiotron 117 A
  F. Choke Coil
B. Fixed Oscillator
  D. Honey Comb coils
  G. Phones
  L. U V 199 Radiotron

by a variable air condenser. In the case of the variable oscillator, the condenser was a General Radio type used in wavemeters. In order to increase the accuracy of the readings, a mirror was mounted vertically at the centre of the dial, so that the dial setting of the condenser could be read by reflected light on a circular scale about 4 feet in diameter, the scale being graduated in millimeters. This type of condenser was supplied with a Vernier control. The small composition knob of it was removed and a 1" pulley substituted. By means of a cord belt and another pulley 5 feet distant, it was possible to tune the condenser without being sufficiently close to introduce body capacity effects.

In the plate circuit a choke coil was inserted to act as an impedance. It consisted of a bundle of iron wires with a large number of turns of No.34 silk covered wire. This served to prevent the passage of the radio frequency currents through the plate circuit.

The fixed oscillator inductance was shunted with a variable condenser whose capacity could be varied to suit the measurement but it was always fixed at a definite value for any one measurement. The telephones used to indicate resonance occupy the same position as the choke coil in the other oscillator and has an impedance of about 2000 ohms.

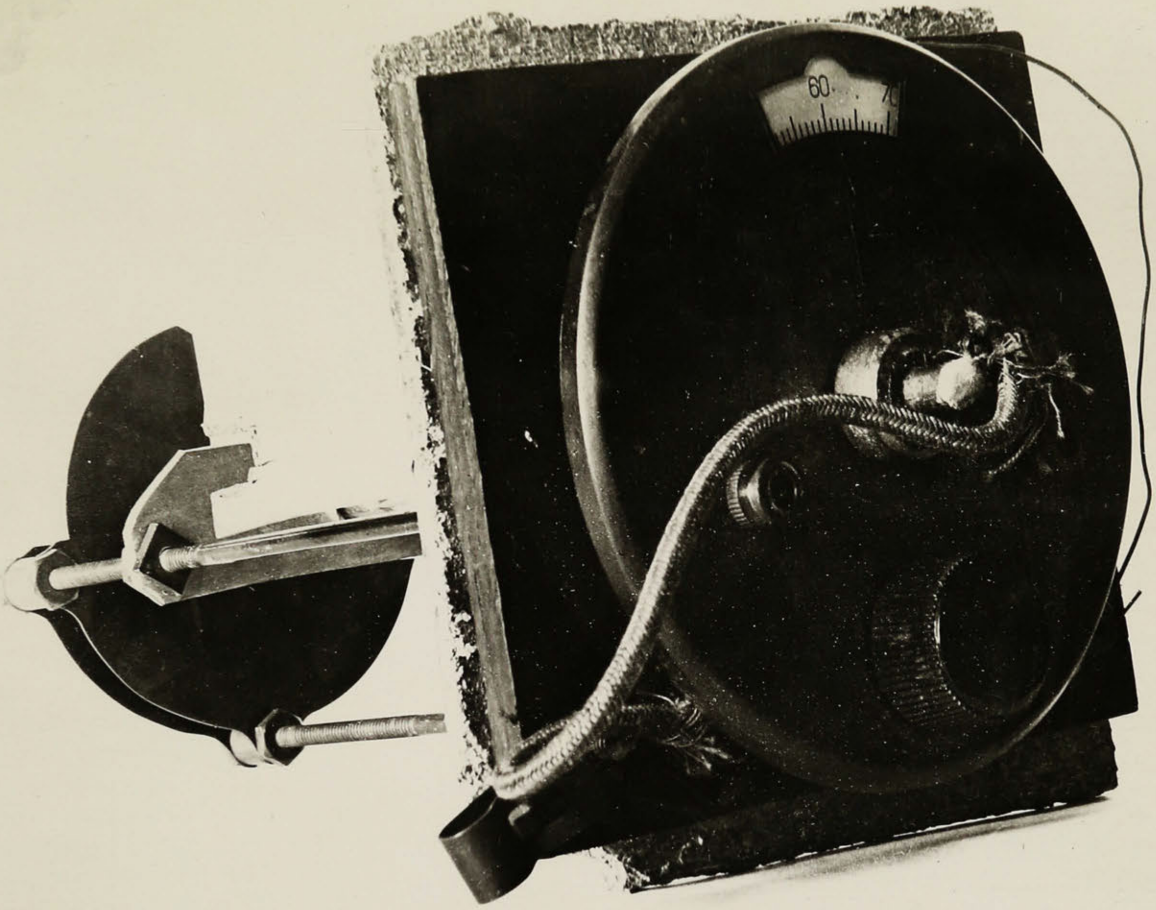
As to the vacuum tubes employed the 217A Radiotron was found excellent for the circuit in which the cell was connected. In this circuit the oscillations have to be forced through substances which show a tendency to absorb and also conduct. If the oscillations are to be intense and steady, considerable power is required. The 217A tube works satisfactorily at from 90-135 volts,, on the plate and 6 volts on the plate filament. Even however with certain substances like water, it was found best to place a capacity in series with the variable condenser. Just exactly how such a condenser functions it is difficult to say with certainty, but at any rate it allows an accurate measurement to be made on substances whose specific conductivity reach a value of 10^{-5} -.

In the fixed oscillator or receiver a U.V.199 Radiotron was successfully used. This requires only a very small filament current and 45 volts on the plate. The success of the method was found to depend very largely on the proper construction of a cell. The ordinary type of two fixed plates has disadvantages, one of the most important being the "capacity lead effects". The cell to be described was constructed on the principle of a variable condenser and could be immersed in the liquid, the container of the liquid acting as a support for the cell.

The Cell

According to the description already given, it would not seem possible to bring the receiver in resonance by means of the tuning condenser, note the reading, connect in the cell and again take the reading. The difference between these values giving the capacity of the cell - The leads however connecting the cell to the condenser have capacity and these must be corrected for. Rather than attempt to make this correction the lead capacity was eliminated.

The cell consisted of two sets of semi-circular plates. One set are fixed and are called the stator plates, and are bolted by means of brass rods to an insulating frame of hard rubber. The other set known as the rotor, are fitted to a brass axle, the position of the axle being so adjusted that they will mesh with the stator plates without touching them. In order to ensure relatively the same position for the two sets of plates, the axle supporting the rotor ones passes through two bearings, one through the insulating frame,



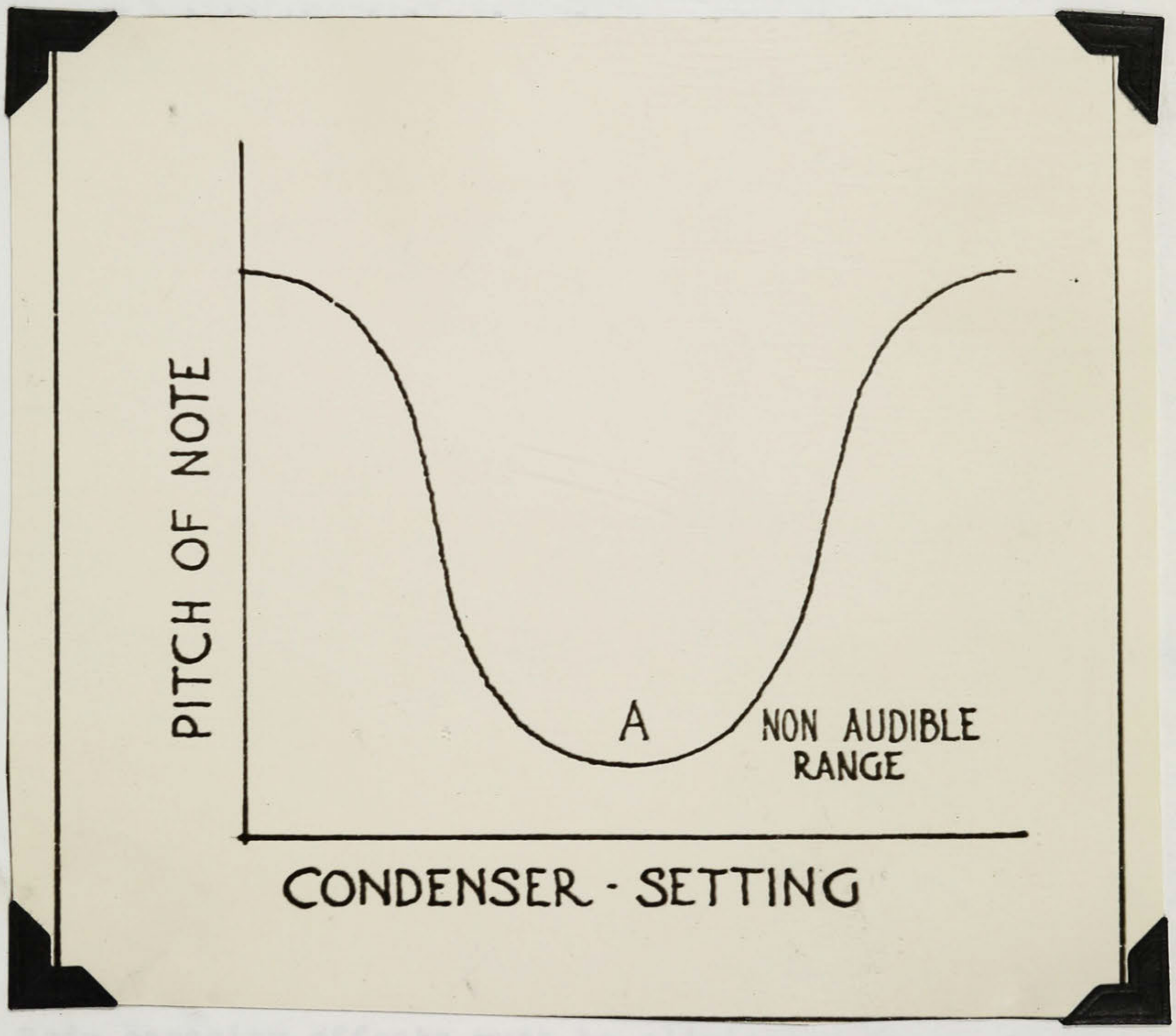
PHOTOGRAPH OF THE DIELECTRIC CELL

the other a short distance above the plates. The latter was attached to, but insulated from the brass rods, as indicated on the diagram. A Vernier dial was fixed to the brass axle. This dial owing to its peculiar construction was capable of rightly fixing the vertical position of the rotor plates and at the same time provided a means of setting the plates at a definite capacity value. The liquid to be measured was placed in a container and the plates of the cell immersed in it; a lid fastened to the insulating frame held it in position.

This type of cell removed any capacity lead effect. In actual use, it was permanently connected in the circuit and set at a definite value as indicated by the dial reading. Tuning of the variable condenser brought the receiver to resonance and the reading was noted.

Operation of Oscillators

In operation, the oscillators are started by lighting the ~~fix~~ filaments of the vacuum tubes. The condenser of R is set at an appropriate value. Radio frequency oscillations are then picked up by tuning the variable condenser in oscillator B and the beat notes heard in the telephones. The whistle fárst heard is represented diagramatically by the following insert:-



The pitch of the note is plotted as co-ordinates the condenser sitting as abscissae - A point A is reached when the note is of too low a frequency to be audible. On either side of A the pitch gradually increases in equal intensity to a condition where it is too high to be audible. A condition of resonance is reached at A.

This condition of resonance can be almost exactly realized if the following factors are taken into account:-

(1) The fixed oscillator oscillates at one frequency only, during a measurement.

(2) The receiver is sufficiently well constructed to give sharp tuning. Each of these points may now be considered in detail. In the first case, vibration must be negligible so that the wiring and coils will not alter their relative positions. Wave lengths which are either multiples or sub-multiples of the natural period of oscillation are called harmonies and must be avoided especially if one at least of the harmonies has a comparable intensity to the fundamental wave. Body capacity effects must be eliminated by operating the tuning at a distance of three or four feet from the oscillator.

In the second case the most important factor is the use of well made apparatus. Poor insulation is the source of most of the trouble to be encountered in this connection.

Calculation of the Dielectric Constant

For purposes of argument, it may be assumed that the capacity of the variable condenser is equal to the area of the rotor which is meshed with the stator plus some constant related to the end effect in the condenser. If the dielectric is air then for two **settings**.

$$C_1 = A_1 + k.$$

$$C_1' = A_1' + k$$

A = area of plates
k = end effect constant.

$$\therefore C_1' - C_1 = A_1' - A_1$$

If the dielectric has a value E, then

$$C_2' - C_2 = E(A_1' - A_1)$$

$$\therefore \frac{C_2' - C_2}{C_1' - C_1} = E$$

The principle is made clear in the following way:

CALCULATION OF DIELECTRIC CONSTANT

Assume the dial setting is 20 and at resonance, the variable condenser reads 60. The cell is now adjusted to a dial reading of 60 and the condenser reading 30 for resonance. A change of capacity of 40 units of the cell corresponds to 30 units of the condenser. If the substance in question was air, then the relative capacity between setting 20 and 60 of the cell equals 30 units. Upon the substitution of some other substance the relative capacity between 20 and 60 becomes 60 units. For sake of clarity this can be summed up in the following manner:

	Cell Setting	Condenser Setting
AIR:	20 units	60 units
	60 "	30 "
SUBSTANCE: X	20 "	70 "
	60 "	10 "

Relative capacity for X = 60

" " air = 30

$$\therefore \frac{\text{Capacity of X}}{\text{Capacity of air}} = 2$$

It has already been shown that $C = \underline{EA}$

for air $C = K$ for a simple condenser

for X $C = EK$ " "

$$\therefore \frac{C_x}{C_A} = E = \text{dielectric constant}$$

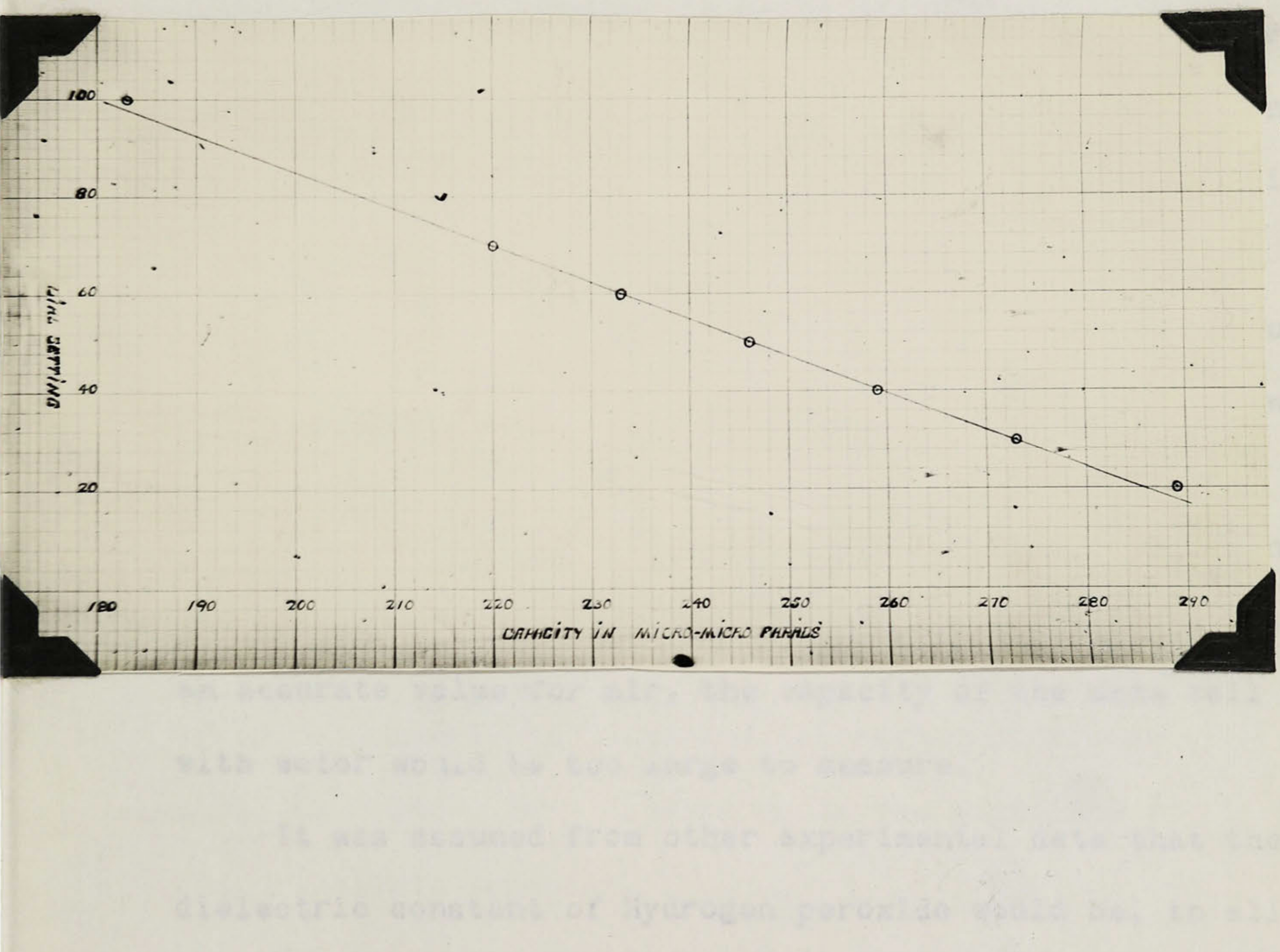
The above explanation makes it evident that the capacity of either the cell or the tuning condenser need not be known in absolute units.

THE RELATIONSHIP BETWEEN DIAL SETTING AND CAPACITY OF A VARIABLE CONDEBSER.

Before the above method for the measurement of dielectric constants can be used, it must be shown that a linear relationship exists between the above quantities. In parallel with the tuning condenser a General Radio Precision Condenser type 222 Serial #44 was connected. The following readings were obtained.

Capacity in Mfd Precision Condenser	Dial Setting Variable Condenser
289	20
270	30
259	40
246	50
233	60
220	70
183	100

Upon plotting these values as the included graph shows, a linear relationship exists between 30° and 80°. A condenser should therefore only be used between these limits. As will subsequently be shown, the same applies to the measurements concerned with the dielectric cell



The curve showing the linear relationship between dial setting and capacity in micro-micro farads of the variable tuning condenser.

itself.

A study of any physical chemical table indicates that the dielectric constant of various substances varies from about unity to one hundred. It is not always practical to directly compare the substance in question to that of air. The reason for this is that either the accuracy in determining air or the substance would have to be sacrificed. Suppose it is desired to measure the dielectric constant of water. The literature gives a value of about 80, using the simple formula, the capacity of the air condenser would be $\frac{A}{4\pi d}$, for water, $\frac{80A}{4\pi d}$ i.e. the capacity of the same condenser,

With water as a dielectric would be 80 times that when air was present. If a large enough condenser were used to give an accurate value for air, the capacity of the same cell with water would be too large to measure.

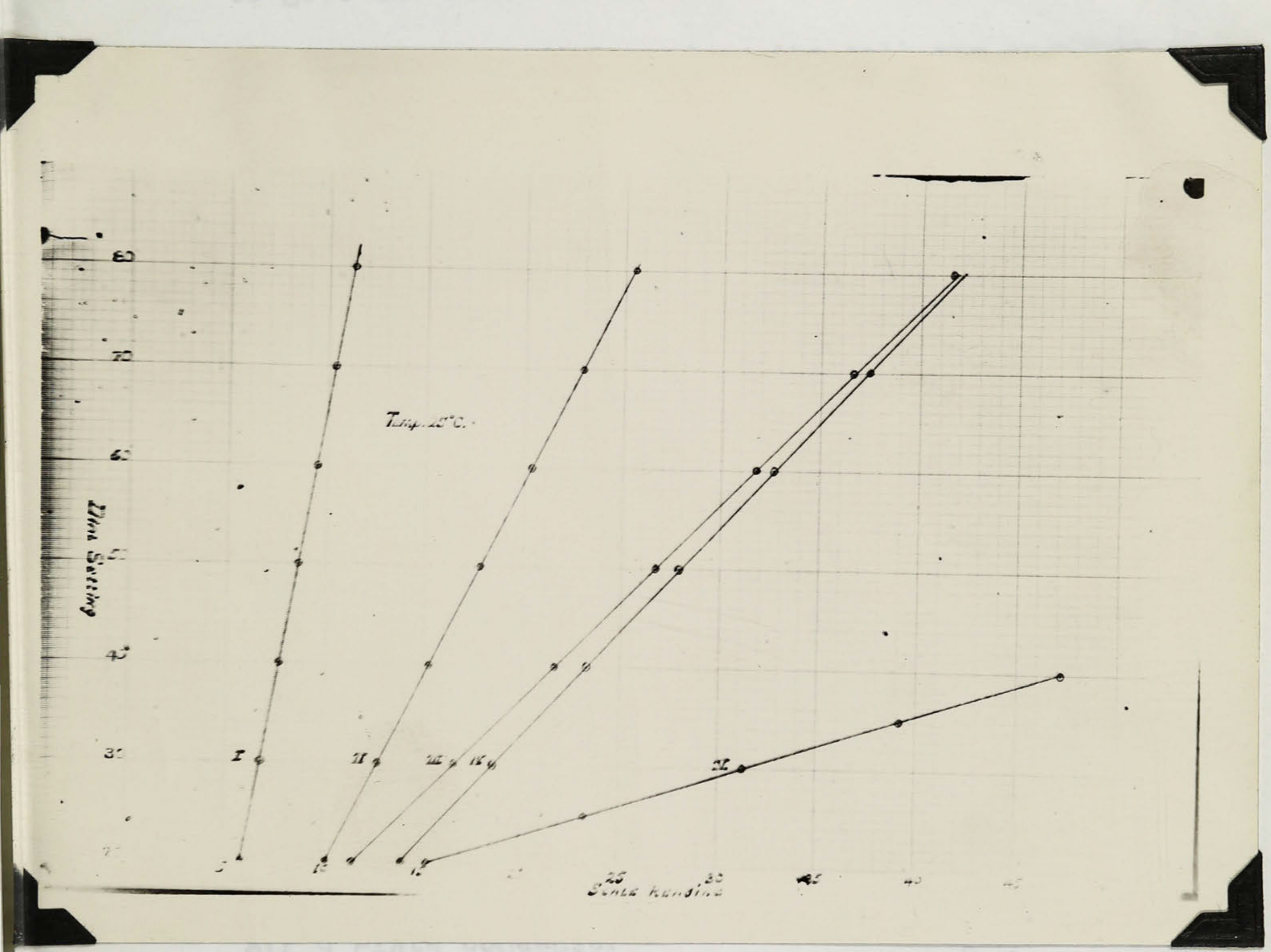
It was assumed from other experimental data that the dielectric constant of Hydrogen peroxide would be, in all, probably of the same order of magnitude as water, and that it (water) would be a convenient standard to use provided its value was accurately known. A glance through the literature indicated that such was not the case and that a re-determination of the value was essential.

THE MEASUREMENT OF THE DIELECTRIC CONSTANT OF WATER AND ITS CHANGE WITH TEMPERATURE.

In order to avoid the difficulty of obtaining an accurate value for either the capacity of the condenser in air or water, as previously stated - "a step by step" method was adoptẻd. The flexibility in design of the cell allowed this to be accomplished readily. The stator plates were held together by means of nuts and were separated by means of washers. The capacity of such a condenser could be conveniently altered in one or both of two ways. Either the stator or rotor plates could be separated further apart, i.e. by a thickness of more than one washer, or the number of stator plates and rotor plates could be increased or decreased in number, i.e. a 3,5,7,9, etc. plate condenser could readily be constructed. If the dielectric constant were small i.e. 2-10, a 7 or 9 plate condenser could be conveniently used and the number of plates could be reduced to 3, according to the magnitude of the dielectric constant.

The following scheme was then employed:

A 9 plate condenser of the dimensions used made possible an accurate determination of chlorbenzene relative to air. A 5 plate was successful in comparing chlorbenzene to nitrobenzene while 3 plates served



The "Step-by-Step" method for the measurement of the dielectric constant is illustrated by the above curves.

The ratio of the $\frac{\text{Slope I air}}{\text{Slope III } C_6H_5Cl}$ = E for C_6H_5Cl

ratio of the slope $\frac{\text{III } C_6H_5Cl}{\text{IV } C_6H_5NO_2}$ = E for $C_6H_5NO_2$

V is used to compare $C_6H_5NO_2$ with water to give the ratio between nitrobenzene and water.

The vernier dial used on the cell was accurately divided into 100 divisions which corresponded to 180°. Instead of merely taking a reading at 20 and moving up to say 80, resonance points were obtained, for 20, 30, 40, 50, 60, 70 and 80 or whatever settings were most convenient. The values for these settings are given in Table I.

Table No.1.

Temp. 25°6.

Air 9 Plate Condenser		C_6H_5CL 9 plate condenser	
Cell Setting	Readings	Cell Setting	Readings
20	5.90	20	11.50
30	6.80	30	16.30
40	7.70	40	21.60
50	8.60	50	26.80
69	9.50	61	31.80
70	10.40	70	36.60
80	11.30	80	41.30

Table #1 continued.

C6 H5 CL 5 Plate Condenser

20	5.20
30	9.80
40	10.30
50	12.80
60	15.30
70	17.90
80	20.45

$C_6H_5NO_2$ 5 Plate Condenser

20	11.25
25	19.50
30	27,70
35	35.50
40	43.15

Nitro Benzene 3 plate condenser

20	3.10
30	7.50
40	12.10
50	16.70
60	21.60
70	26.30
80	30.70

Water 3 plate condenser

20	11.50
25	16.55
30	21.35
35	26.40
40	31.40
45	36.50
50	42.00
55	46.90

Water 3 plate condenser 0°C

20	7.30
25	12.80
30	18.60
35	20.30
40	30.20
45	35.20
50	41.70
55	47.10

Water 3 plate condenser 50°

20	4.30
25	8.90
30	13.45
35	18.00
40	22.60
45	27.20
50	31.80
55	36.80

Table #1 continued.

WATER 3 plate Condenser 75°	
20	6.30
25	10.50
30	14.45
35	18.80
40	23.00

Curves 1 and 2 represent the relative capacity of air and chlorbenzene using a 9 plate condenser; 3 and 4 that of chlorbenzene and nitrobenzene, for a 5 plate condenser; 5 and 6 nitrobenzene and water with a 3 plate condenser. The values of the dielectric constants can easily be computed for each set as in every case the value is inversely proportional to the slope pf the line obtained by plotting the setting of the condenser against capacity.

$$\text{Dielectric Constant of Chlorbenzene} = \frac{\text{Slope air}}{\text{Slope Chlorbenzene}}$$

$$= 5.61 - = E$$

$$\text{For Nitrobenzene } E = \frac{\text{Slope Chlorbenzene}}{\text{Slope nitrobenzene}} \times 5.61$$

$$= 35.20 \qquad -$$

For Water $E = \frac{\text{Slope Nitrobenzene}}{\text{Slope Water}} \times 35.20$

$= 75.40$

The above values are given for 25°C.

In order to check the constant for water, the value was determined in another way. With a 5 plate condenser a comparison was made between air and ether, with a 3 plate between ether and water. The values are given below.

Table #2

Cell Setting	Readings	Cell Setting	Readings
Temp. 25°6 Air		Ether.	
20	8.44	20	8.34
30	9.46	30	12.60
40	10.58	40	17.36
50	11.76	50	22.38
60	12.92	60	27.02
70	14.10	70	31.64
80	15.26	80	36.12
90	16.40		

E for Ether at 25° $= \frac{2.17}{.540} \times 1 = 4.02$

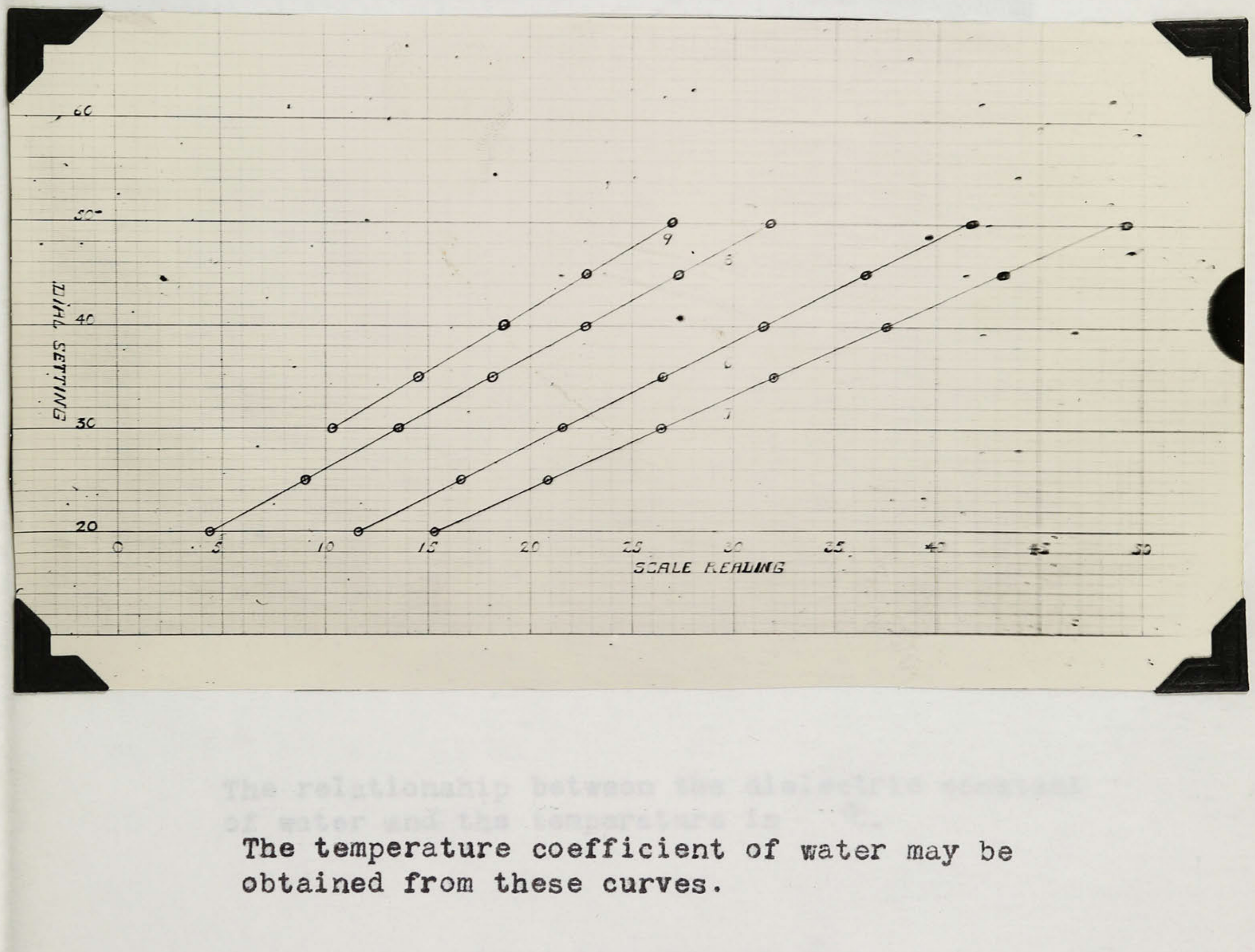
Ether		Water	
20	11.40	30	
30	12.14	30	12.43
40	12.60	40	21.78
50	13.08	50	30.53
60	13.56	60	39.33
70	14.05	70	48.50
80	14.55		
90	15.00		

$$E \text{ for Water at } 25^{\circ} = \frac{5.25}{.280} \times 4.02 = 75.5$$

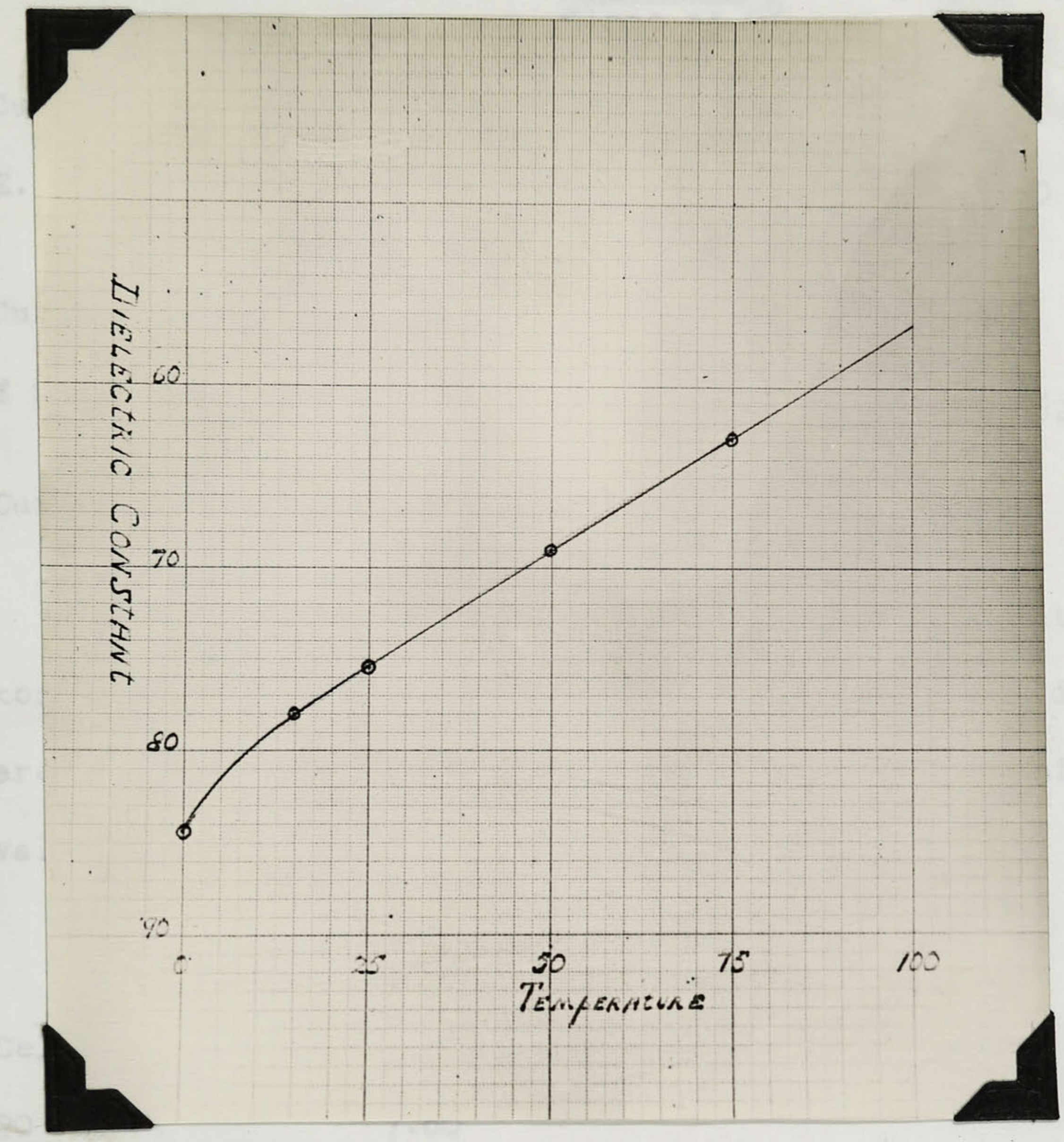
A direct comparison was also made between air and benzene, air and ether. The dielectric constant of benzene was 2.28, that of ether 4.02 - at 25°C

THE TEMPERATURE COEFFICIENT OF WATER

The value for Water at 25°C has been established as 75.40. It was interesting to see in this case what effect temperature had on the dielectric constant. Using the 3 plate condenser which gave the value for water at 25°C, the others were obtained at 0°C, 15°C 50°C and 75°C. All that was necessary was to bring the water to the required temperature and note the change in capacity for various dial settings at resonance. In the same way as before. (See Table I).



The temperature coefficient of water may be obtained from these curves.



The relationship between the dielectric constant of water and the temperature in °C.

$$\text{E. for water at } 0^{\circ}\text{C} = \frac{\text{Slope at } 25^{\circ}}{\text{Slope at } 0^{\circ}} \times 75.4 = 84.4$$

Curve No.7.

$$\text{E. for Water at } 50^{\circ} = \frac{\text{Slope at } 25^{\circ}}{\text{Slope at } 50^{\circ}} \times 75.4 = 69.0 \text{ -}$$

Curve No.8.

$$\text{E for water at } 75^{\circ} = \frac{\text{Slope at } 25^{\circ}}{\text{Slope at } 75^{\circ}} \times 75.4 = 62.9$$

Curve No.9.

The curve showing the relationship between dielectric constant and temperature is given. The measurements in Table 111 are included as checks on water at 0°C, and to obtain the value at 15°C.

Water Temperature 25°

Cell Setting	Readings	
20	7.80	
25	12.15	(Slope - 1.063
30	16.95	
35	21.80	
40	26.60	
45	31.20	

Water Temperature 0°C

20	10.90	
25	16.10	
30	21.50	Slope .946 -
35	27.00	

40	32.20
45	37.20
50	42.30 -

Dielectric Constant Water at 0° C = $\frac{1.063}{.946} \times 75.4$

= 84.7

TABLE #2

WATER TEMPERATURE 25° C

Cell Setting	Readings		
20	5.40		
30	12.05	Slope	1.475
40	19.00		
50	25.90		
60	32.70		
70	39.40		
80	46.05		

TEMPERATURE 15°C-

20	8.60	
30	15.75	
40	23.00	Slope = 1.4150
50	30.00	
60	37.05	
70	44.00	
80	51.00	

	TEMPERATURE O°C	
20	12.80	
30	20.60	
40	28.10	Slope = 1.325
50	35.40	
60	42.80	
70	50.20	

Taking the dielectric constant of water at 25°C = 75.4 -

Then its value at 15° $= \frac{1.475}{1.445} \times 75.4 = 78.5$

at 0° $= \frac{1.475}{1.335} \times 75.4 = 83.5$

A comparison with the values obtained by other investigations is given below:

Substance	Temp °C	E by Resonance Method	E from Landolt Bornstein Tables	**Wave Length**	Author
Benzene	25	2.28			
"	18		2.288	Infinite	Turner
"	19		2.26	73 cm	Drude
"	25		2.273		Isnardi
			Ether		
Ether	25	4.02			
"	18		4.368	Infinite	Turner
"	0		4.68	Infinite	Abegg

(Continued)

Substance	Temp. °C	E. by Resonance Method	E. from Landott-Born-stein Tables	Wave Length	Author
		Chlorbenzene			
Chlorbenzene.	25	5.60			
	25		5.628	600 metres	Smythe
	10.8		10.95	Infinite	Veley
		Nitrobenzene			
Nitrobenzene	25	35.20			
	0°		41.0	Infinite	Abegg
	15°		37.8	Infinite	"
	17°		34.0	73 cm	Drude
	30°		35.1	Infinite	Abegg
	24.5		34.5		Mayder
		Water			
	25o	75.4	-		
	18°	77.2	81.1	Infinite	Turner
	17o	77.6	81.	50 cm.	Rukop
	0	84.4	88.2	75 cm	Drude
			76	Infinite	Cohn & Arons
			80	"	Smale

Five of Niven's[20] values are compared to the values obtained by the resonance method.

Temp.	Niven's Values	Temp.	E. by resonance method
0°	90.36	0°C	84.4
7°	80.06	15oC	78.5 -
33°	69.31	25oC	75.4
58°	59.5	50°C	69.0
83°	37.97	75°C	62.9 -

Discussion of Results

In discussing the results it might be pointed out that the wave length is considered infinite if greater than 10^4 cm. In all cases where the wave length is expressed in cm. the method of standing waves has been employed.

The dielectric constants for benzene show no discrepancy beyond that to be expected i.e. 1%. Since Smythe[21] has found no change in the dielectric constant with the temperature, the values as given are therefore comparable. That of I Shardi is 2.273[22] is often taken as a standard in place of air so that the value of 2.28 is probably accurate to 1/2 of 1%.

The agreement is not so perfect in the case of ether. If, however, one assumes the values of Turner and Abegg to be approximately correct, then on allowing for a temperature coefficient the value at 25o would be 4.25.

In the case of chlorbenzene the constant of 10.95 given by Veley is in error. Smythe's value at the same temperature is in good agreement.

For Nitrobenzene all that need be remarked is that since a direct comparison was made with chlorbenzene (the accuracy ofwhich is fairly well established from Smythe's work), the value 35.2 may be considered correct.

As to water, it is to be noted that the resonance method values are somewhat lower on the average. However, the temperature coefficient is so important in water that in the case of the latter two values obtained by Cohn & Arons and Smale they are valueless for purposes of comparison.

Niven's results for water check reasonably well for temperature up to 25° - above this the deviation is large. As the values above 25° do not fall reasonably well on a smooth curve, it was concluded they were inaccurate. The included temperature curve appears to fall off rather rapidly below 25°C but is linear above this temperature. When this was first obtained some doubt was felt as to its accuracy. Upon checking the values no difficulty was experienced in repeating the values above room temperature, but considerably below. After a number of determinations the curve as given was chosen as correct. See Table No.3.

At high temperatures for water it was often noticed the beat note was weak. This can only be attributed to the higher conductivity of the water probably to be connected with its increased dissociation. In this connection it is worth noting that a pure tin container was found most satisfactory.

One other question might be considered here - the effect of frequency on the value of the constant. It appears logical to presume that if the wave length were considerably shortened, a decrease in the order of magnitude of the constant is to be anticipated. This point of view does not appear to be substantiated from a consideration of preceding table. It is hoped however that the resonance method used over a wide band of wave length will show changes in the value. In the measurements referred to above, the wave length was about 200 metres.

The DIELECTRIC CONSTANT OF HYDROGEN PEROXIDE.

When the measurement of the dielectric constant of hydrogen peroxide was attempted, two difficulties were met with - ease of decomposition and conduction. The first of these was overcome after considerable amount of experimenting by constructing a cell (similar to the one described previously) from block tin. The second was found to be due to traces of the inhibitor which subsequent purification did not completely remove. The method for its removal was fully discussed in Section 1 and will not be repeated here. It is sufficient to say that where the specific conductivity is greater than 10^{-5} accurate results are not obtainable.

In carrying out the determinations the values for peroxide were referred to water as a standard at 0°C . This temperature was chosen because the tendency towards decomposition is then minimized. For the same reason it was found advisable to make only two cell settings viz. at 20 and 80, making possible a rapid determination of the value. If the measurement was not carried quickly, it was found that tiny bubbles formed on the plates after a period of about 5 minutes.

First of all, the cell was calibrated with water i.e. the relative capacity for water between 20 and 80 known. The same was then determined for the various aqueous solutions of peroxide and the dielectric constant calculated in the following manner.

Relative Capacity H202 Soln x 84.4 = E. for H202 Soln -

Relative capacity water.

CAPACITY VALUES FOR HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS RELATIVE TO WATER.

Temp. 0°C

% H202	Cell Setting	Relative Capacity	Water Values
99.45	80-20	33.20	31.30
	"	33.30	31.50
	"	33.30	31.40
	"	33.20	31.70
	"	33.30	31.60
	"	33.50	31.50
	"	33.10	
	"	33.30	
	"	33.30	
Mean		33.28	31.50
		------	------

	% H202	Cell Setting	Rel.Capacity	Water Values
(2)	98.87		34.85	32.10
			34.70	32.05
			34.65	32.30
			34.65	32.10
				32.10
	Mean		34.71	32.11
(3)	81.27		34.85	
			38.50	
			38.60	
			38.75	
			38.80	
			38.90	
	Mean		38,67	32.11
(4)	63.80		41.50	
			41.40	
			41.30	
			41.35	
	Mean		41.39	32.11

	%H202	Cell Setting	Relative Capacity Temp. 0°C	Water Values
(5)	50.23	80-20	43.20	31.70
			43.25	31.60
			43.35	31.90
			43.20	31.80
			43.20	31.60
				31.70
		Mean	43.24	31.71
(6)	43.25	60-20	31.20	22.20
			31.0	22.40
			31.1	22.40
			30.8	22.20
			31.7	22.20
			31.3	
		Mean	31.0	22.32
(7)	36.30	60-20	31.80	
			31.80	
			31.80	22.32
		Mean	31.80	22.32
(8)	32.0		31.70	
			31.70	
			31.50	
			31.30	
			31.50	22.32
		Mean	31.54	22.32

% H_2O_2	Cell Setting	Relative Capacity	Water Values
		Temp. 0°C	
9) 25.8		30.70	
		30.70	
		30.60	22.32
	Mean	30.67	22.32
10) 20.80	60.20	30.00	29.7
		29.70	
		30.30	22.32
	Mean	30.00	22.32
11) 14.00	80-20	43.40	33.80
		43.00	33.70
		43.70	33.70
		43.50	33.60
		43.50	33.60
	Mean	43.42	33.62
(12) 6.9	80-20	37.70	
		37.20	
		37.40	33.62
	Mean	37.40	33.62

CALCULATION OF THE DIELECTRIC CONSTANTS

% H202	
99.45	$\frac{33.28}{31.50} \times 84.4 = 89.2$ -
98.87	$\frac{34.71}{32.11} \times 84.4 = 91.2$
81.27	$\frac{38.67}{32.11} \times 84.4 = 101.6$ -
63.80	$\frac{41.39}{32.11} \times 84.4 = 108.8$-
50.23	$\frac{43.24}{31.71} \times 84.4 = 115.0$ -
43.25	$\frac{31.0}{22.32} \times 84.4 = 116.2$ -
36.30	$\frac{31.80}{22.32} \times 84.4 = 121.1$ -
32.0	$\frac{31.54}{22.32} \times 84.4 = 119.0$ -
25.80	$\frac{30.67}{22.32} \times 84.4 = 116.0$ -
20.80	$\frac{30.00}{22.32} \times 84.4 = 113.5$
14.20	$\frac{43.42}{33.62} \times 84.4 = 108.5$
6.90	$\frac{37.40}{33.62} \times 84.4 = 94.0$

The relationship between percent hydrogen peroxide and dielectric constant is shown in the included curve.

DISCUSSION OF RESULTS

The fact that the curve passes through a maximum was

The dielectric constants of Hydrogen peroxide and its aqueous solutions.

hardly to be expected. It might have been anticipated had the Solvent been one of low polarity, such as ether. Under the circumstances the accuracy of the experimental results might be doubted. That the method itself is applicable is evidenced from the results already given for water and some organic liquids. If the apparatus was actually giving misleading results the error must exist either in the cell, or impurities in the peroxide must be masking the true values.

The peroxide however was obtained from that used in the determination of the 99.45 and 99.87% values. This peroxide which had been crystalized three times was diluted with distilled water whose conductivity was low enough to prevent any error. In the next section its value will be given. Further, the water used for dilution was the same as that for the cell calibration.

An investigation as to the probability of the cell giving misleading results was also instituted. Observation showed that a very slight decomposition occurred. This gave rise to a thin film of bubbles on the tin plates of the condenser. Analytically the amount of decomposition over a period of two hours could not be detected. If this were the cause of abnormalities the value would be lowered, not raised. The following experiment will prove this. The three values for 20.8% H_2O_2 have already been given. The measurements were made in about five minutes. The solution was allowed to stand two hours in the cell and another reading taken. Bubbles of oxygen were distinctly evident on the plates. The readings are given below:

Cell Setting	Relative Capacity	
60-20	30.00	) Time Interval)
	29.70	) about five minutes)
	30.30	)
	26.40	after two hours.

Other instances of the same phennmenon were observed.

The possibility of a thin layer of tin oxide on the condenser plates was also investigatdd. Readings for water were taken before and after they had been cleaned with fine emery paper. The results obtained were:

Cell Setting	Relative Capacity	
60-20	22.20	before cleaning
"	22.40	after "

CALIBRATION OF CELL

It is also to be noted the capacity values for water changed quite noticeably. For #1 the calibration value for water is given as 31.50 for the 20-80 setting. For 2,3, and 4, 32.11 was considered most correct, which amounts to a variation of 2%. For #5 the value re-determined was 31.7. As the capacity values for 6, 7 and 8, 9 and 10 were large - a range of 20-60 was used - 22.32 was taken as correct throughout these measurements. Upon determining water for the 14 and 7% solutions 33.62 proved correct. The reason for this is that the cell being constructed of a soft metal like tin may at various times have been sufficiently bent or twisted to account for these variations.

The variations do not come into comparative measurements since the cell was not subjected to any strain when a comparison was made between water and peroxide measurements. A survey of the results would however indicate that for any one set of comparative readings the error is about 1%.

THE REFRACTIVE INDICES OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AND THE CALCULATION OF THEIR ELECTRICAL MOMEMTS.

Inasmuch as a close relationship exists between the dielectric constant of a substance and the refractive index, it was considered valuable to find in this case if the refractive indices would show abnormalities similar to those observed in the case of the dielectric constant.

As mentioned in the early part of this section an approximate method for the calculation of the electrical moment is possible when both dielectric constant and refractive index data are available. In order to make these two constants comparable the refractive index was extrapolated for infinitely long waves by means of the Cauchy Formula. The accuracy of this extrapolation is extremely doubtful because of the probability of the existence of absorption bands in the infra red. The calculation of the moments has been done, however, mot from the standpoint of the actual numerical values obtained but rather to test the applicability of the Debye equation to highly associated liquids.

EXPERIMENTAL METHOD

The Spectrometer or goniometer is a convenient instrument to use for this purpose. It consists essentially of a divided circle about the axis of which a collimator and telescope can rotate. The rays of light enter the collimator and after passing through a lens form a parallel pencil. These rays are refracted by a prism mounted vertically on the centre of the divided circle. The amount of refraction is determined by means of the telescope.

The source of light was a hydrogen tube which made possible the measurement of the refractive index for three wave lengths by focusing in turn on the Hydrogen lines 6563, 4861, 4340, which appear as red, blue and green images on the cross hairs in the telescope eye-piece. The prism was identical with that used by Maass and Hatcher. The formula connecting the quantities whose values have to be known in order to find N the refractive index is

$$N = \frac{\sin \frac{A+d}{2}}{\sin \frac{A}{2}}.$$

where A = angle of the prism, d = angle of minimum deviation.

PROCEDURE

The angle A is first determined. The prism is adjusted so that the rays reflected from one of the faces produce an image of the slit of the collimator coinciding with the cross wires in the field of view. The telescope is then fixed and the prism table rotated until an image of the slit again coincides with the cross line. The angle turned through = 180° - A.

The solution in question is then poured into the hollow prism and its position fixed so that one face is parallel to the collimator slit. The telescope is connected by means of a set screw to the rotating disc. It is then moved to a position where one of the images coincides with the cross hairs, and also where on further rotation of the disc the image turns and moves in the opposite direction. This is the position of minimum dutation.

The position of the telescope is also noted whan the prism is removed and of course is a constant = K. The difference between the position of minimum duration and the K gives d, - Focussing on the other two images permits the determination of d_2 and d_3.

$$N_1 = \frac{\sin \frac{A + (d_1 - K)}{2}}{\sin \frac{A}{2}}$$ for red line = 6563

$$N_2 = \frac{\sin A + (d_2 - K)}{\sin \frac{A}{2}}$$ for green line = 4861

$$N_2 = \frac{\sin \frac{A \ (d_3 - K)}{2}}{\sin \frac{A}{2}}$$ for blue line 4340

Temp. 24.5°C

H. Line	% H202	Angle of Minimum Duration	Prism Angle	N
6563	13.85	22° 46¼'	57° 24'	1.3409
4861		23° 15'	"	1.3476
4340		23° 32½'		1.3515
		------		-------
	35.48	23° 50¼'		1.3557
		24° 19'	"	1.3623
		24° 32'		1.3657
		------		------
	55.60	24° 53'	57°22½'	1.3701
		25° 22'	"	1.3768
		25° 42½'		1.3814
		------		-------
	74.79	25° 57	57° 24'	1.3851
		26° 27¼		1.3914
		26° 43½'		1.3984
		-------		-------
	89.36	26° 46¼'		1.3957
		27° 24½'		1.4032
		27° 46'		1.4091

The refractive indices for each wave length were then plotted against concentration. The values at 20, 35, 50, 60, 80, 100 were read off each of the three curves. The following values were obtained in this way:

Temp. 24.5°C

% H202	N. for H Line		
	6563.	4861.	4340
20	1.3445	1.3515	1.3560
35	1.3552	1.3623	1.3672
40	1.3584	1.3600	1.3710
60	1.3735	1.3808	1.3863
80	1.3885	1.3955	1.4020
100	1.4030	1.4105	1.4175

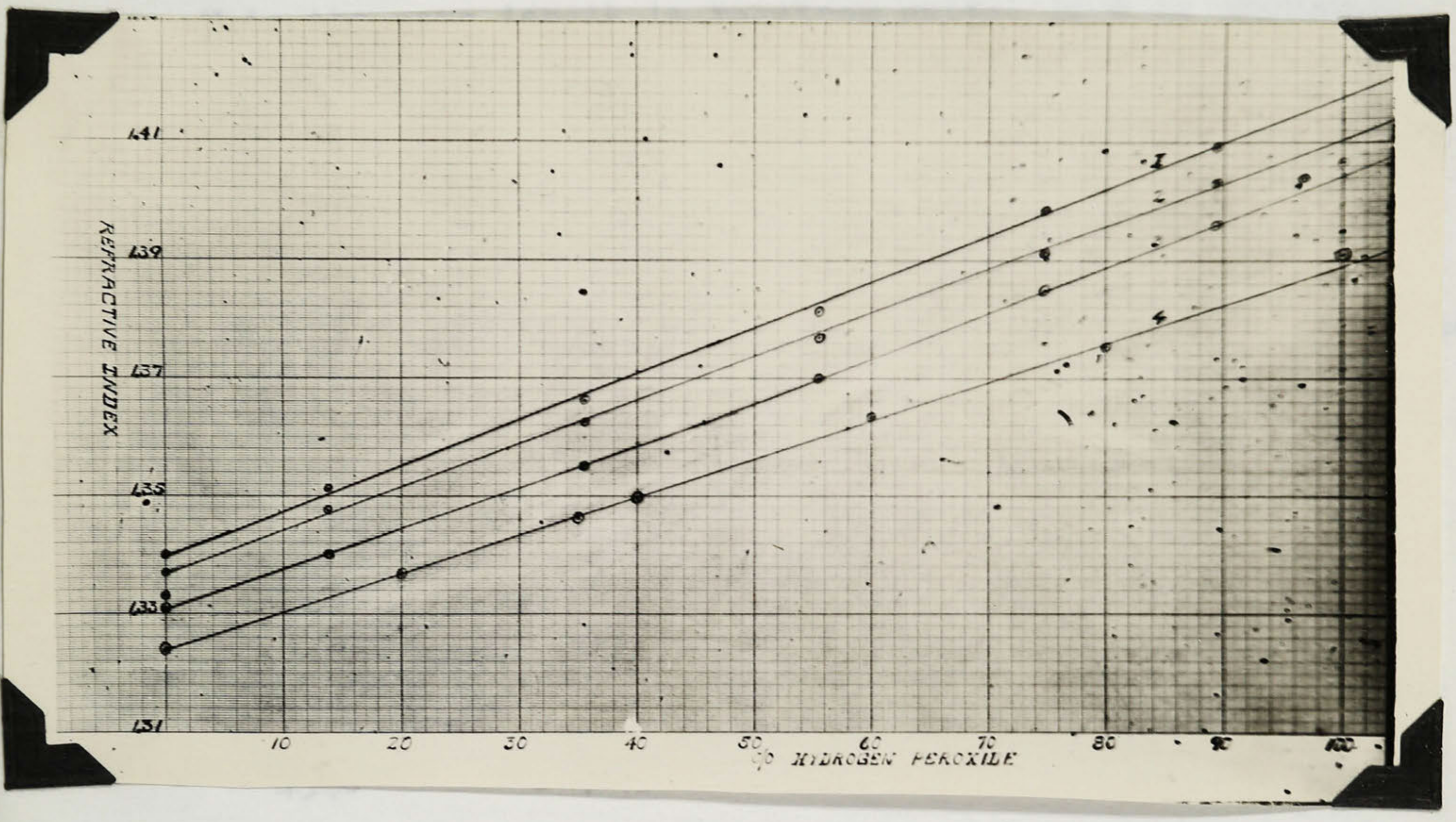
EXTRAPOLATION OF THE REFRACTIVE INDEX TO AN INFINITE WAVE LENGTH

The Debye equation relating ~~to~~ the dielectric constant to the molecular refraction of a substance, may be represented since $\frac{4\pi}{3} N_A \mu' = MR_\infty$

$$\frac{E-1}{E\ 2} \quad \frac{M}{d} = MR_\infty + \frac{4\pi N \mu^2}{9KT}$$

It is evident that if MR_∞ be known an approximate method is available for the calculation of μ. To do this use is made of the Cauchy formula which relates the refractive index of a substance to the wave length at which it is measured. i.e.

$$N-1 = A(1+\frac{B}{W^2})$$



The refractive Indices of aqueous solutions of Hydrogen Peroxide -

Curve No. 1 represents the refractive indices for the 4340 H line

Curve No. 2 - - - for the 4860 H "

" No. 3 - - - " 6563 H "

" No. 4 - - - " refractive indices extrapolated to infinite wave length - by means of the Cauchy formula.

N is the refractive index, A and B are constants.

W is the wave length in Angstrom units. If W is infinite N-1 = A. In order to obtain N two values of the refractive index are required at & W, and W_2 wave lengths. The wave lengths chosen were 6563 and 4340.

A calculation is given to indicate how N_∞ is obtained.

CALCULATION OF N for 100% H2O2

$$N - 1 = A\left(1 + \frac{B}{W^2}\right)$$

N for 6563 line = 1.4030

" 4340 = 1.4175

$$\therefore \quad .4030 = A\left(1 + \frac{B}{(6563)^2}\right)$$

$$.4175 = A\left(1 + \frac{B}{(4340)^2}\right)$$

Therefore $.4030 + \frac{.4030}{(4340)^2}B = .4175 + \frac{.4175}{(6563)^2}B$ -

$$B = 1.145 \times 10^6$$

Then $.4030 = A\left(1 + \frac{1.145 \times 10^6}{(6563)^2}\right)$

$$A = .3910 -$$

$N-1 = .3910 \quad \therefore \quad N_\infty = 1.3910$ -

Similarly N_∞ was obtained for the solutions. Knowing N_∞,

MR_∞ can be calculated i.e. $\frac{N^2_\infty - 1}{N^2_\infty + 2} \frac{M}{d} = MR_\infty$.

The following results were obtained.

% H202	N_∞	MR_∞
20%	1.3360	3.854
35%	1.3460	4.110
40%	1.3495	4.154
60%	1.3637	4.533
80%	1.3756	4.964
100%	1.3910	5.643

CALCULATION OF THE ELECTRICAL MOMENT OF PURE HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTION.

Sufficient amount of data is now available to calculate the electrical moments of Hydrogen peroxide, and its aqueous solutions. The density of the solutions at 0° and 24.5°C is given by Maass and Hatcher. M the molecular weight can be calculated.

A calculation of μ for a 20% solution is given.

From the curve for the dielectric constant

$E = 113$ Density at zero 1.080

$MR = 3.854$ $K = 1.37 \times 10^{-16}$ $T = 273$

$N_A = 6.06 \times 10^{23}$ $M = 19.88$

$$\therefore \text{ Of } \frac{E-1}{E\ 2}\ \frac{M}{d} = MR\infty + \frac{4\pi N_A \mu^2}{9KT}$$

we have -

$$\frac{112}{115} \times \frac{19.88}{1.080} = 3.854 + \frac{4 \quad \times 6.06 \times 10^{23}}{9 \times 1.37 \times 10^{-16}} \ \mu^2 \times 273$$

$$= \frac{\left(\frac{112}{115} \times \frac{19.88}{1.080} - \times 3.854\right)(9 \times 1.37 \times 10^{-16} \times 273}{4\pi \times 6.06 \times 10^{23}}$$

= square root of above expression

= 2.80×10^{-19}

The following values were obtained:

% H202	
20	$.78 \times 10^{-18}$
35	$.79 \times 10^{-18}$
40	$.80 \times 10^{-18}$
60	$.80 \times 10^{-18}$
80	$.83 \times 10^{-18}$
100	$.86 \times 10^{-18}$

THE MOMENT OF WATER

Two methods are available in this calculation since both the temperature coefficient and molecular refraction for infinitely waves are known. The refraction index method will be discussed first. Using the 6563 and 4340 hydrogen lines MR_α is found to be 3.610. Using the appropriate constants for water is calculated as $.78 \times 10^{-18}$.

Under the heading of "Experimental Verification of the Debye Theory" a method of determining μ is given depending on the temperature coefficient of the polarizability. For purposes of comparison the calculation of the moment from this standpoint is included. The equation is $PoT = a + c\ T$ where

$PoT = \frac{E-1}{E\ 2}\ \frac{M}{d}\ T$, A and C are constants

obtained from a curve where PoT values are plotted as ordinates and T as abscissae. (Using the values of E already given at various temperatures PoT can be obtained.)

PoT	Temp. °A
$\frac{83.4}{86.4} \times \frac{18}{1} \times 273 = 4746$ -	273
$\frac{77.5}{80.5} \times 18 \times 288 = 4991$ -	288
$\frac{74.4}{77.4} \times \frac{18}{1} \times 298 = 5157$	298
$\frac{68}{71} \times \frac{18}{.99} \times 323 = 5637$	323
$\frac{62}{65} \times \frac{18}{.97} \times 348 = 6160$	348

The value of a obtained from the curve = 237.6

$$\mu^2 = \frac{237.6 \times 9 \times 1.37 \times 10^{-16}}{4\pi \times 6.06 \times 10^{-23}}$$

$$\mu = .20 \times 10^{-18}$$

$$C = \frac{4\pi}{3} NAU' = MR_\infty = \text{slope of the line}$$

∴ MR was found to be 1.64 . The correct value is 3.61

In order to compare the various values obtained for the moments of peroxide and water they are listed below.

	μ calculated from MR and E	μ calculated for water from Temperature co-efficient of E
Water	$.78 \times 10^{-18}$	$.2 \times 10^{-18}$
20% H_2O_2	$.78 \times 10^{-18}$	
35 "	$.79 \times 10^{-18}$	
40 "	$.80 \times 10^{-18}$	
60 "	$.80 \times 10^{-18}$	
80 "	$.83 \times 10^{-18}$	
100 "	$.86 \times 10^{-18}$	

DISCUSSION OF RESULTS AND THE STRUCTURE OF WATER AND HYDROGEN PEROXIDE.

The curves relating refractive index to concentration show no abnormalities as observed in the dielectric constant determination. The same holds true for N   plotted against concentration. All the values fall approximately on continuous gently sloping lines and the largest deviation occurs in the case of the blue line for H2 viz 4340. This is undoubtedly due to the experimental error because the blue image was not as well defined as the other two and therefore increased somewhat the difficulty of focussing the cross hairs of the telescope on it.

Maass and Hatcher[23] obtained 1.4140 for the refractive index of pure peroxide with sodium light and 1.4043 for96.81%. From the values given that of sodium light ought to be 1.4064 as the dotted curve shows. The refractive index at 97% does however fall on this curve. On recalculating the value for pure peroxide from the prism angle and angle of minimum deviation given by them, it was found to be 1.4063. 1.4140 as given is in all probability due to an arithmetical error. The refractive index was also determined by Bruhl.[24] He obtained values ranging 1.4005 to 1.4069. The upper limit of his determination is about the correct one.

As the molecular refraction of a substance is both an additive and a constitutive one, it is interesting to see what light it throws on the constitution of peroxide. The use of the Lorenz. — Lorenz formula gives

$$R = \frac{1.4064)^2 - 1}{(1.4064)^2 + 2} \times \frac{34}{1.439}$$

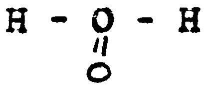
$R = 5.805$.

If R. for water = 3.715

" " Hydrogen = 1.050

Then R for O H = 2.665

If Hydrogen peroxide consists of two OH groups linked by a single bond i.e. HO-OH, 2 x OH = 5.330 compared to 5.805 as calculated. The latter values point to unsaturation. Either of the two following formulae are possible. $HO \equiv OH$ or



$$H - \underset{\overset{\|}{O}}{O} - H$$

The molecular refraction of quadrivalent oxygen in pyrone salts as measured by Miss Homfray[25] is equal to 2.7

R for 2 Hydrogens = 2.10

R " 2 O = $\underline{5.4}$ 7.60

The calculated value for HO = O H is then 7.60

For a divalent oxygen linkage one obtains R for Hydrogen = 2.10

R " O = $\underline{4.58}$

6.68

The value for H - O - H is 6.68

DISPERSIVE POWER AND CONSTITUTION

Due to the researches of Bruhl the specific dispersive power is represented in the following way:

$$\frac{N_\gamma^2-1}{N_\gamma^2+2)d} - \frac{N_\alpha^2-1}{(N_\alpha^2+2)d}$$

and the molecular dispersive power is

$$\frac{N_\gamma^2-1}{N_\gamma^2+2}\,\frac{M}{d} - \frac{N_\alpha^2-1}{N_\alpha^2+2}\,\frac{M}{d}$$

$= M_y - M_\alpha$ By putting $N_y = 1.4175$ and $N_\alpha = 1.4030$, $M_y - M_\alpha$ give .0175. The atomic dispersions for the lines are .036 for H_2 and .019 for hydroxylic oxygen.

The calculated value for hydrogen peroxide would then be:

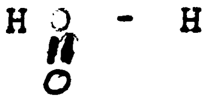
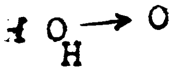
$2 \times H_2 = 2 \times .036 = .072$

$2 \times O_2 = 2 \times .019 = \underline{.038}$

Calculated value .110

Observed " .175

Neither the refractive power nor dispersive power of hydrogen peroxide offers decisive proof as to the correct formula for this substance. Some evidence of value may however be obtained by a consideration of Sugden's[26] parachor. On the basis of the following formulae the calculated value of the parachor is given.

		Parachor Calculated	Parachor observed
(1)	$HO-OH$	74.1	69.6
(2)	 $H\underset{\underset{O}{\|}}{O}-H$	97.7	
(3)	 $H\underset{H}{O}\rightarrow O$	72.5	

The calculated value for the parachor corresponding to

(3) most nearly approahhes the observed value of 69.6. This formula represents what is termed a co-ordinate link, i.e. the electrons shared by the two oxygen atoms come from the oxygen atom attached to the two hydrogen atoms.

It appears reasonable then to suppose that the calculated values of the molecular refractive and dispersive power of hydrogen peroxide would agree, were the atomic refraction of a co-ordinate linked oxygen atom known. On the basis then of the deviations shown in all three cases for formulae 1 and 2, 3 is to be taken as correct.

ELECTRICAL MOMENT

The calculation of μ has been shown by many investigators to hold unqualifiedly for gases. For liquids this is subject to a restriction. If the molecules with permanent moments are completely free to move and have their dipole strength unaltered in the liquid state through combinations, then the law must hold for both. If the liquid is one in which the molecules tend to associate, that is, join in groups of two, three or more molecules then as the temperature changes ~~then~~ the dipole strength is altered and the law does not apply. At lower temperatures the association tends to annihilate the permanent moment resulting in much too small a quantity in the calculated value.

In both the water and the peroxide solutions the calculated values are small viz. $.80 \times 10^{-18}$. It obviously has little significance so far as a physical constant is concerned but it may be considered as strong evidence for association in the above cases.

From the above considerations and those alone, it is possible to make certain statements about the degree of association. Using the principle that every system tends to a condition of minimum potential energy, every type of association will tend towards that molecular arrangement with which a minimum amount of energy is concerned. If the complex were di molecular the most stable configuration would be a straight line, if tri-molecular that of an equilateral triangle. Beyond this stage the configuration would be difficult to foresee.

If the formation of double molecules were complete one should have instead of N_a molecules of moment μ contributing $N_A \mu^2$ to the molecular polarization. $\frac{N_A}{2}$ molecules of moment 2μ, contributing $2 N_A \mu^2$ or twice the original factor.

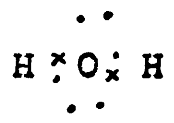
In the case of a tri molecular condition a configuration of the type of an equilateral triangle would result in a zero value.

If the value of the moments have any significance the most logical thing would be to presume that most of the molecules of water and hydrogen peroxide exist in the tri-molecular condition, or that at any rate an equilibrium condition exists between the di and tri molecular condition, and also that simple molecules of either water or peroxide are scarce.

The application of the electronic mechanism of valency to the structure of water and hydrogen peroxide.

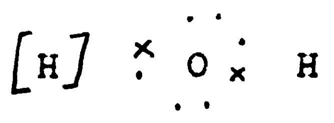
This question can best be introduced by considering the much disputed question as to whether hydrogen should be classed with the alkali metals or with the halogens. Hydrogen consisting of a nucleus of one proton and attendant electron can lose an electron easily, acting therefore like an alkali metal. It appears however capable of taking one up either by sharing or forming a negative ion.

Water may then be represented by any one of three formulae, u



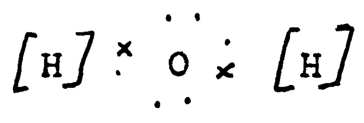
$\mathrm{H}\,{}^{\times}_{\cdot}\,\overset{\cdot\,\cdot}{\underset{\cdot\,\cdot}{\mathrm{O}}}\,{}^{\cdot}_{\times}\,\mathrm{H}$

1



$[\mathrm{H}]\;{}^{\times}_{\cdot}\;\overset{\cdot\,\cdot}{\underset{\cdot\,\cdot}{\mathrm{O}}}\;{}^{\cdot}_{\times}\;\mathrm{H}$

11



$[\mathrm{H}]\;{}^{\times}_{\cdot}\;\overset{\cdot\,\cdot}{\underset{\cdot\,\cdot}{\mathrm{O}}}\;{}^{\cdot}_{\times}\;[\mathrm{H}]$

111

The first formulae represents two co-valent linkages - the second a co-valent and an electrovalent linkage - the third two electrovalent linkages.

The first formula could be interpreted to mean no shift of electrons takes place. Such a molecule is typically "normal" and non-polar.

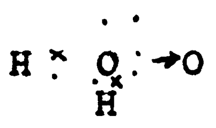
The second is unsymmetrical and a shift of an electron occurs. Such a configuration is typically "abnormal" and polar.

Though the third formula has two electron shifts, the symmetry would prevent polarity similar to the example previously discussed for nitro-methane and tetranitromethane. Formula 2 is probably correct for water.

THE FORMULA FOR H_2O_2

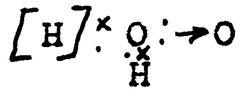
The formula $H\underset{\overset{\|}{O}}{O}H$ seems reasonable from two points of view. Firstly, it gives the closest agreement between the observed and calculated values for the parachor. Secondly the ease with which oxygen splits off is in entire agreement with such a configuration.

From the standpoint of electron valencies the following formulæ are possible -



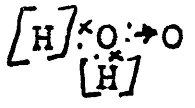
$H\overset{\times}{\cdot}\underset{\overset{\times}{H}}{\overset{\cdot\cdot}{O}}\!:\rightarrow O$

1



$[H]^{\times}\!\cdot\underset{\overset{\times}{H}}{O}\!:\rightarrow O$

11



$[H]^{\times}\!\cdot\underset{\overset{\times}{[H]}}{O}\!:\rightarrow O$

111

In 1 the two hydrogen atoms are linked by co-valencies to 1 oxygen. A coordinate link exists between the two oxygen atoms. In 11 one H atom has an electrovalent linkage ; in 111 both H atoms have electrovalent linkages. The high dielectric constant, high degree of association and the properties of a weak acid point to formula 11, as the most probable.

Section 111

THE CONDUCTIVITIES OF POTASSIUM CHLORIDE AND ACETIC ACID IN HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS.

GENERAL INTRODUCTION:

By far the largest part of the experimental data substantiating the ionic hypothesis has been obtained from observations made in aqueous solutions. To merely state that water is an abnormal liquid is not an explanation, because others just as abnormal in a number of their physical properties do not possess the ability in conjunction with acids, bases or salts to form highly conducting media. It is probably correct even to say that the theory of electrolytic dissociation is the theory of the dissociation of acids, bases and salts in water.

The reason for the specificivity in the theory is not far to seek - few solvents giving rise to comparable conductivities are known. It is at once evident then, that the use of some solvent other than water, yet quite similar in properties would be valuable in showing or at least indicating what properties of water were mest predominant in determining its ability to give rise to dissociation of the above mentioned chemical types.

Hydrogen peroxide appeared to offer striking possibilities. Maass and Hatcher[27] and Maass and Matheson[28] have already shown that the lowering of the freezing point of peroxide by salts was of the same order of magnitude as in water. Hence it was argued ionization must be of the same order. Further if the dielectric constant and ionization are related as Nernst and J.J.Thomson believe, it is only logical to assume that comparable magnitudes are to be expected in peroxide to those in water.

The value of such measurements having been decided a difficult problem presented itself, viz. the methdd of measurement. Obviously a commonly used conductivity cell with platinized electrodes is uut of the question, for both decomposition and polarization must be avoided.

The first of these difficulties could be overcome as learned from previous experience by using tin electrodes. If however tin electrodes are substitued and the ordinary bridge method employed, polarization is still a factor which has to be taken into consideration. Both of these difficulties were satisfactorily overcome by measuring the drop of potential across two tin electrodes with a quadrant electrometer.

In order to make a just comparison with water conductivities were carried out in aqueous solutions and pure peroxide using as the solute a strong electro- KCL and a weak one - acetic acid.

EVIDENCE FOR AND FACTORS GOVERNING IONIZATION

As evidence of a comparable dissociation in hydrogen peroxide to that in water the lowering of freezing paint may be used. The following figures are given for different substances.

Substance	% Solute	Solvent Water	Solvent Peroxide
		Temp	Lowering
Cane Sugar	20	2.5	2.6
Na Cl	15	11.5	12.1
$Na NO_3$	20	8.5	9.0
$Na_2 SO_4$	4	1.2	1.6

The above figures taken from the determinations of Maass and Hatcher indicate that the lowering of the freezing point is about the same as in water. Again the molecular weights determined by the freezing point method show the same abnormalities as for water.

Solute	Ratio $\frac{\text{calculated M wt}}{\text{theoretical M wt}}$
Water	1.26
Cane Sugar	.90
Sodium Chloride	.53
Sodium Nitrate	.56
Sodium Sulphate	.35

On analogy with water then it is to be expected that a comparable ionization takes place.

The high dielectric constant of water is supposed to be a hint as to the cause of its great ionizing power when controlled with other solvents. The following examples are chosen to make the comparison clear.

	Water	Methyl Alcohol	Ethyl Alcohol
Dielectric Constant	80	34	26
% Ionization $\frac{N}{10}$ K I	88	52	25
" " $\frac{N}{10}$ NaBr	86	60	24
" " $\frac{N}{10}$ CH_3 cook	83	36	16

The explanation as to how a high dielectric constant favors ionization is as follows: (#)

If we take the view that the forces which hold the atoms in molecules are electrical in origin it is evident

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(#) Mellor Inorganic Chemistry page 479.

that these forces will be very much diminished when the molecule is close to the surface of or surrounded by a conductor or a substance possessing a high dielectric constant. Thus if A and B represent two atoms in a moleculer placed near a conducting sphere, the effect of electricity induced on the sphere by A will be represented by an opposite charge A^i, inside — the image of A in the sphere. If A be considered as the positive charge very near the outer side of the sphere, A^1 opposite in sign beomes nearly the same value. The presence of the sphere then, tends to annihilate the electrical field of A. If it is an electrical field which tends to hold A and B together, then the presence of a conducting sphere weakens the forces between them. This same effect is believed by J.J. Thomson[29] to be the case when the molecules are surrounded by a substance of high dielectric constant, so that when molecules having their electrical charges segregated caused by electro-valent linkages, are dissolved in water the forces between the constituent atoms is sufficiently weakened to give rise to charged atoms known as ions.

A somewhat similar conception is possible by assuming that electrolytes under all conditions are to some extent ionized. The force between the ions in the molecule is given by $F = \frac{e^2}{E R^2}$ the letters having the same significance as in Section 11. If E is small F the force of attraction tending to give rise to the molecular condition is large. If E is large the force of recombination is then small, so that in water most of the solute molecules exist in the ionic condition.

In point of fact, however, the mechanism of ionization is by no means as simple as the above outlined theory assumes. In the first place, it is extremely improbable that any simple mathematical expression applies over short distances, and, secondly, complicating factors arise when it is considered that ionization is actually a property of neither the solvent or solute, but both.

Finally then it can be said that although plenty of evidence is available to indicate that ions do exist, the factors governing ionization are by no means understood.

Owing however to the fact that dielectric constants of aqueous solutions of peroxide are considerably higher than those of water, the relationship between them and the conductivity of salts, offers a means for checking the assumption used to explain the peculiar qualities of water in this respect.

EXPERIMENTAL METHOD

Two essentially different methods are available for the determination of the resistance of liquids. For this purpose they may be referred to as the static and the alternating current bridge method. In the static method ~~of~~ polarization at the electrodes is avoided by measuring a drop of potential across two electrodes while in the alternating current bridge methods the conditions of the experiment are so arranged as to make it negligible.

Due to the mistrust with which Kohlrausch's conductivities were originally received, the comparative accuracy of the two methods was investigated by a number of workers in the field notably Ostwald, Tollinger, Bouty and Foussereau. 30

In every case the agreement was within the limits of experimental error.

As none of the static methods differ in principle from the one to be described here, they have been purposely omitted.

In outline the apparatus consisted of a glass cell, into which four tin electrodes could be inserted. A current of the order of .001 amperes was passed through the solution, the circuit was made by means of the two outer electrodes which will be termed the primary ones. A quadrant electrometer connected to the other two (secondary electrodes) made possible the measurement of the potential difference between two fixed points in the solution. By means of a double throw switch connected to the electrometer and across a resistance box which is in series in the primary circuit it was possible to measure the drop of potential across both the fixed electrodes and the known resistance. The ratio of the Quadrant Electrometer readings in the two cases made possible the calculation of the resistance of the solution in question since the same current is flowing through both.

In detail the glass cell was simply a U tube with two other glass tubes sealed into the horizontal portion and in the same plane as the two outer arms. In the ~~primary~~ outer arms the primary electrodes were inserted while the drop of potential was measured across the two inner ones by means of the electrometer Q. The current was supplied by a number of dry cells and passed through the resistance Box R and solution on closing the switch S. The double switch R could quickly measure the P.D. across E.E. or R. Due to the fact that the Quadrant Electrometer often is difficult to manipulate, a short account of it is considered pertinent.

Essentially a quadrant electrometer consists of a shallow cylindrical metal box divided into four quadrants - opposite quadrants are connected together. A light aluminium vane is suspended by either a conducting quartz fibre or phosphor bronze wire so that it hangs symmetrically inside the box. The upper end of the suspension terminates in a set screw to which a battery may be attached so as to charge the vane to a potential of about 90-135 volts. In operation if the two pairs of quadrants be connected to two bodies at different potentials the vane is deflected to that pair of quadrants which are at the lower potential. This deflection is indicated by means of a mirror attached to the vane suspension and in this case was reflected on a scale 2 metres distant. The mathematical relationship between the deflection and the potentials of the Quadrant and needle is -

$$\theta = k \left(V - \frac{v_1 - v_2}{2}\right)(v_1 - v_2)$$

Where = deflection V = potential of the vane v_1 and v_2 respective potentials of the quadrants.

When V is large $\theta = kV(v_1 - v_2)$ - and since V is constant $\theta = k_1 (v_1 - v_2)$

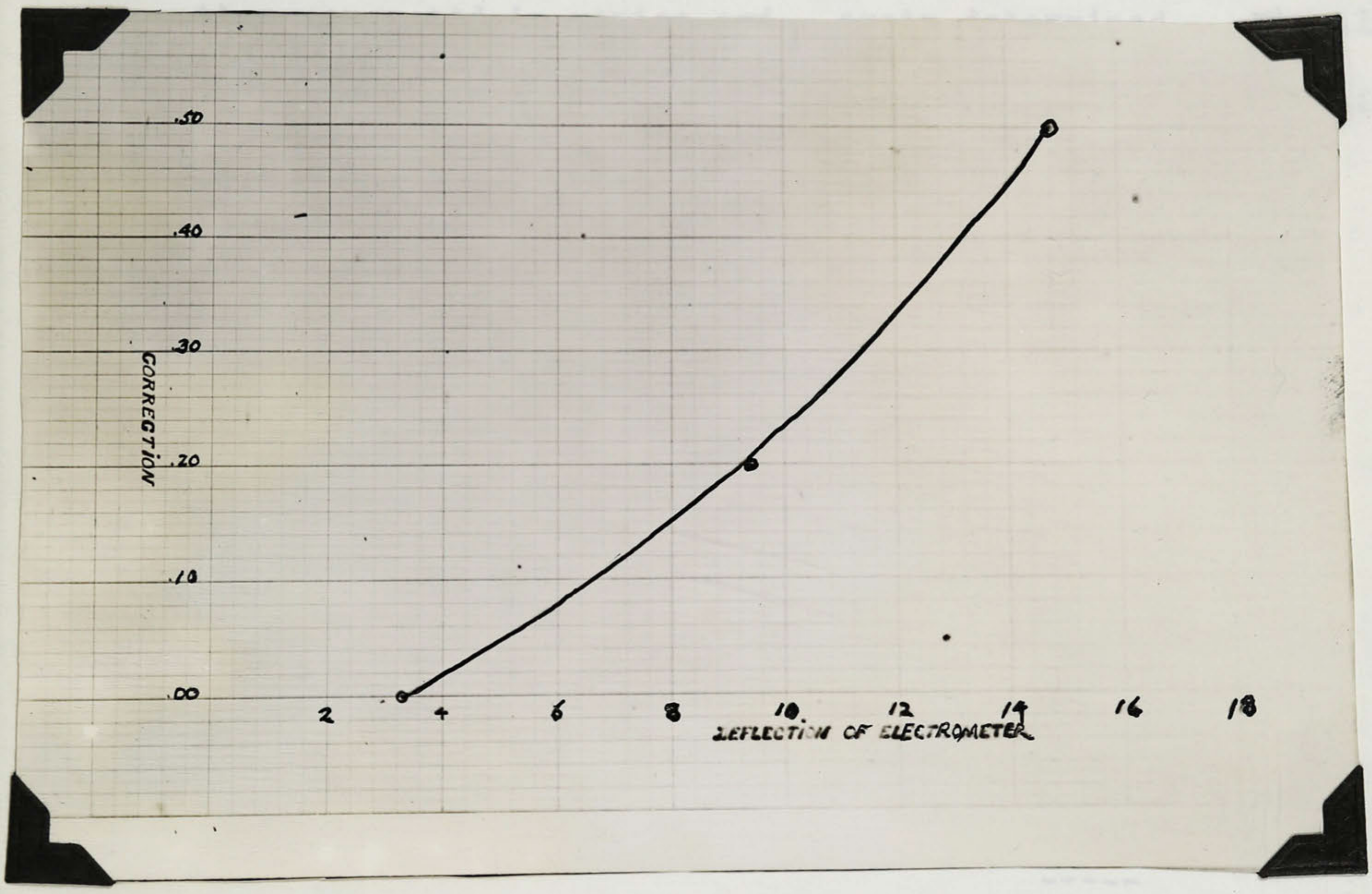
If one pair of quadrants is earthed say v_2, $v_2 = 0$

Then $\theta = k_1 v_1$. This relationship was the one used in subsequent measurements.

Certain operations are necessary in order to satisfactorily use the instrument. Stray currents, insulation leakages and vibration must be avoided. In order to eliminate all three of these the metal case was grounded and the electrometer was placed on a heavy sheet of glass in turn supported by a solid stone top table. As to the sensitivity, this will of course depend on the type of work for which the electrometer is to be used. Quartz suspensions are troublesome and are to be avoided wherever possible. The biggest objection is the difficulty in making a good electrical connection between the fibre and the vane on the one hand, and the point of suspension on the other. A light phosphor bronze wire can be used where high sensitivity is not demanded and the difficulty of obtaining good electrical contact is removed. For conductivity measurements the latter suspension was found to give good results.

THE SCALE CORRECTION OF THE DEFLECTION

Owing to the irregularities in the semi-circular scale and the position of the electrometer relative to it, the scale deflections were not exactly proportional to the potential differences measured. The following method of correction was applied. 3 dry cells were used.



The correction to be applied to the deflection of the Quadrant electrometer.

Each in turn was connected across the quadrants of the electrometer and the deflection determined in all 3 cases. Two were then connected in series and again determined. Finally the deflection was noted for all three in series. The calculation of the error will make the method clear.

(1) The scale deflection for each dry cell was found to be 4.60.

(2) Two were connected in series = 9.40
If function were linear = 9.20
∴ Error = .20

(3) Three were connected in series = 14.30
For a linear relation = 3x4.60 =13.80
∴ Error = .50

The error was plotted against deflection as shown in the accompanying graph and the correction made in each set of measurements.

DETERMINATION OF THE CELL CONSTANT

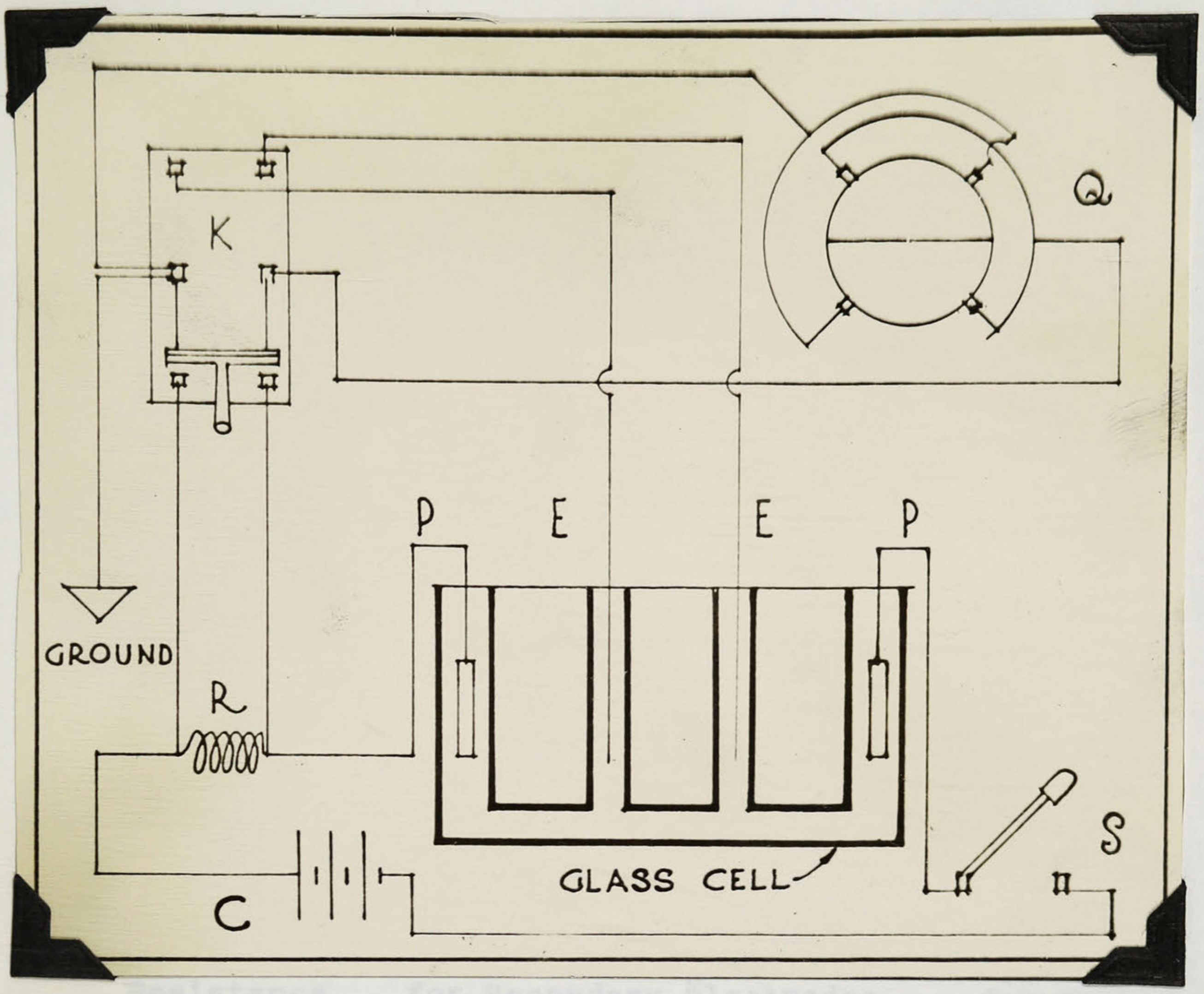
The method employed in this case will illustrate the general method employed in the conductivity measurements. N/10 KCL was first employed for calibration. This solution was poured into the cell and the four tin electrodes placed in position. The two outer electriaes were connected in the circuit of the cell C and the resistance R. R had a value of 22000 ohms. The secondary electrides were connected to one pair of end terminals of the double throw switch K while the other two shunted the resistance R. One of the centre terminals was connected to ground, the other to one pair of quadrants, the other pair of quadrants were grounded. The switch K was thrown in turn across the secondary electrodes E E and the resistance R and the Scale Readings noted. A table of results is included. The letters refer to the accompanying figure.

Temp. 20°C

N/10 KCL

Resistance	for secondary electrodes	for resistance
22000 ohms	4.06	14.11
Correction to scale	.04	.46
Corrected Readings	4.02	13.65

Resistance of Cell = $\frac{4.02}{13.65}$ x 22000 = 6471 ohms



The Static Method for measuring Conductivities of Electrolytes

E. E. Secondary electrodes
P. P. primary "
C battery of dry cells
R - known resistance
K - double throw switch
S - single " "
Q - quadrant electrometer

Resistance of cell   Specific Resistance

$\therefore$ $R \propto r$ or $R = Kr$ where K = cell constant

The specific conductivity $C = \frac{1}{r}$ where r = specific resistance

$\therefore$ $R = \frac{K}{C}$ or $K = R\,C$

The specific conductivity of $\frac{N}{10}$ KCL at 20oC = 1.17×10^{-2}

$\therefore$ $K = 6471 \times 1.17 \times 10^{-2} = 75.82$

As a check the cell constant was also determined with N/100 KCL

Resistance	for Secondary Electrodes	for Resistance
22000	16.00	5.80
Correction to Scale	.57	.08
Corrected Readings	15.42	5.72

Resistance of Cell = $\frac{15.42}{5.72} \times 22000 = 59300$ ohms

$\therefore$ Specific Conductivity of N/100 KCL = $\frac{75.82}{59300} = 1.278 \times 10^{-3}$

Landoldt Bornstein gives 1.278×10^{-3} . Actually the agreement cannot be expected to be better than 1/2%.

It might be mentioned here that in a series of measurements involving the same cell and electrodes, any change in the position of the secondary electrides was obviated by having the electrodes of such a length that they did not reach the main body of the liquid in the horizontal portion of the cell.

RESULTS

Conductivity of acetic acid in 22.2 6% hydrogen peroxide.

As the conductivity of acetic acid in peroxide was expected to be low from analogy with water, the aqueous solution was purified as carefully as possible. After a number of distillations a product was obtained having a specific conductivity of 3.56×10^{-6}. Even with a solvent of the above mentioned conductivity corrections had to be applied to the values obtained. This correction depends on the fact that the solvent and solute act like two resistances in parallel. The resistance of the solution is related to that of the solvent and solute,

$$1/R \text{ Solution} = 1/R \text{ Solute} + 1/R \text{ Solvent}$$

or specific conductivity of the solution = conductivity of solute + conductivity of solvent.

The following results were obtained for acetic acid at 0°C.

Approximate Normality.	% H_2O_2 22.26	Specific Conductivity Uncorrected	Specific Conductivity Corrected.	Mol. Cond.	Dilution in litres
2N	"	$6.48\text{x}10^{-4}$	$6.44\text{x}\ 10^{-4}$	.315	.486
1N	"	$5.05\text{x}\ 10^{-4}$	$5.01\text{x}\ 10^{-4}$	.757	1.200
$\frac{N}{10}$	"	$1.78\text{x}\ 10^{-4}$	$1.74\text{x}\ 10^{-4}$	2.090	12.00
$\frac{N}{50}$	"	$7.70\text{x}\ 10^{-4}$	$7.34\text{x}\ 10^{-5}$	4.40	60.00
$\frac{N}{100}$	"	$5.48\ \text{x}10^{-5}$	$5.12\text{x}\ 10^{-5}$	6.14	120.0
$\frac{N}{500}$	"	$2.45\text{x}\ 10^{-5}$	$2.09\ \text{x}10^{-5}$	12.5	600.0
$\frac{N}{1000}$	"	$2.05\text{x}\ 10^{-5}$	$1.69\text{x}\ 10^{-5}$	20.3	1200.0

Conductivity of KCL in 22.26% Hydrogen Peroxide 0°C

Approz.Normality	% H_2O_2	Spec.Cond.	Mol.Cond.	Dilution in Litres
2N	22.26	$9.62\text{x}10^{-2}$	48.1	.500
1N	"	$5.36\text{x}10^{-2}$	54,7	1.020
$\frac{N}{10}$	"	$1.26\text{x}\ 10^{-2}$	62.8	5.00
$\frac{N}{25}$	"	$2.64\text{x}10^{-3}$	69.5	25.0
$\frac{N}{50}$	"	$1.41\text{x}\ 10^{-3}$	70.5	50.0
$\frac{N}{100}$	"	$7.63\text{x}\ 10^{-4}$	76.3	100.0

Conductivity of KCL in 35.48% Hydrogen peroxide. 0°C

The Specific Conductivity of the solvent was found to be 2.0×10^{-5}. Although this value is about ten times that of the former solution no correction factor need be applied for KCL.

Approximate Normality	% H_2O_2	Spec.Cond.	Mol. Cond.	Dilution in litres
1 N	35.48	4.84×10^{-2}	53.3	1.10
$\frac{N}{10}$	"	5.88×10^{-3}	59.3	10.10
$\frac{N}{500}$	"	6.30×10^{-4}	67.6	107.3

Conductivity of Acetic Acid in 90.2% Hydrogen peroxide 0°C

This aqueous solution was purified to an extent where the conductivity reached a value of 2.2×10^{-6}

% H_2O_2	Spec. Cond.		Mol Cond.	Dilution
	Uncorrected	Corrected		
90%	2.44×10^{-5}	2.22×10^{-5}	.020	.901
"	1.23×10^{-5}	1.01×10^{-5}	.0570	5.64
"	8.30×10^{-6}	6.1×10^{-6}	1.66	273.0

Conductivity of KCL in 90.2% Hydrogen Peroxide 0° C

The same solution was used as in the case of the acetic acid determinations.

Approximate Normality	% H_2O_2	Spec.Cond.	Mol.Cond.	Dilution in litres
1N	90	5.00×10^{-2}	50.8	1.016
$\frac{N}{10}$	"	6.15×10^{-3}	55.9	9.083
$\frac{N}{100}$	"	7.73×10^{-4}	63.2	82.10

Conductivity of KCL in 100% Hydrogen Peroxide.

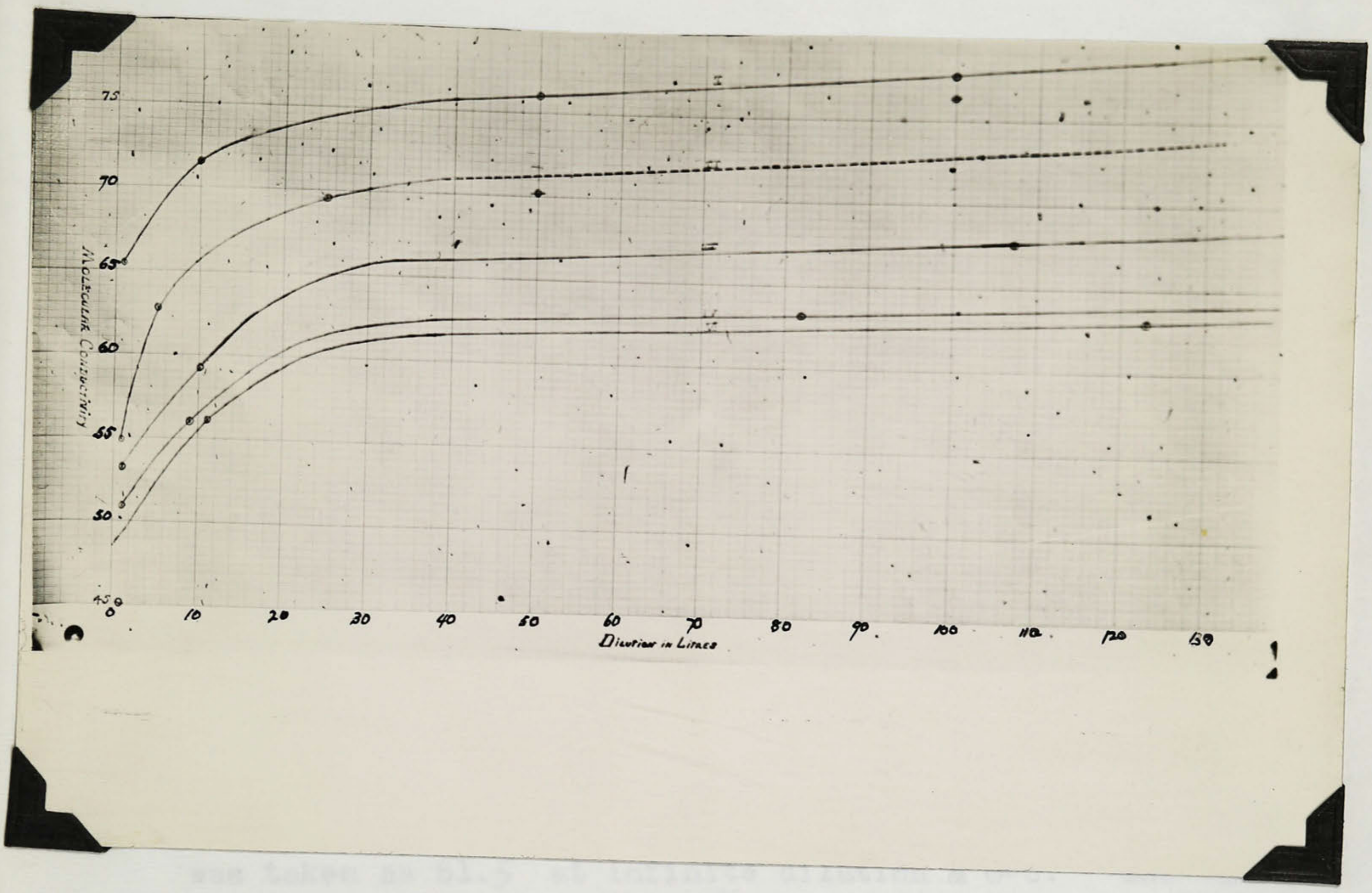
The peroxide used for this purpose was preserved for about four months by keeping it frozen by means of solid carbon dioxide. It was found that the conductivity was high even after a crystallization, the value being about 1.4^{-4} As a result the values had to be corrected.

% H_2O_2	Spec.Cond.		Mol. Cond.	Dilution in litres
100%	Uncorrected	Corrected		
"	4.51×10^{-2}		44.8	.995
"	5.25×10^{-3}	5.11×10^{-3}	56.3	11.1
"	6.52×10^{-4}	6.12×10^{-4}	63.0	123.0

DISCUSSION OF RESULTS

Probably the most satisfactory method to discuss the conductivities of KCL and acetic acid in aqueous solutions of hydrogen peroxide is to compare them with those of water. For this purpose a series of curves is included to show the relation between the molecular conductivity and dilution for KCL. The curves for water and 22.26, 35.48, 90.2 and 100% $H2O_2$ are all of the same type as water. Further as the percentage of H2O2 increases the molecular conductivity for any one dilution, decreases regularly. It might have been expected that the 35.47% H_2O_2 solution would show abnormalities comparable with the dielectric constant. Such however does not appear to be the case. The fact also that the dielectric constant of all the solutions is higher than in the case of water, it would be anticipated that all of the solutions would show a higher value with respect to specific or molecular conductivity than water.

The ionizing power however with which the value of the dielectric constant is presumably most directly connected is best investigated by determining the ratio of the molecular conductivity at any dilution with that at infinite dilution. To



A comparison is made between the molecular conductivity of **K C L** in water and dilution to aqueous solutions of peroxide of 22, 35, 90 and 100% concentration.

Curve No. 1 is for water
No. 2 22% peroxide
No. 3 35% "
No. 4 90% "
No. 5 100% "

accurately calculate by extrapolation methods the molecular conductivity at infinite dilution necessitates the specific conductivities of solutions of from N/1000 to N/10000. Such data is not available from the present measurements. In order to approximate to this value for the various solutions the following method was resorted to. The molecular conductivities were plotted against per cent peroxide for dilutions of 10, 20, 40 and 100. The included curves show a distinct break in the curve for all dilutions at about 40% hydrogen peroxide.

The value of the molecular conductivity of KCL in water was taken as 81.5 at infinite dilution & 0°C. and the curve was drawn, by proportionality considerations, to those obtained at dilutions of 10, 20, 40 and 100. In this way then an approximation to the conductivities at infinite dilution is possible.for the four aqueous solutions, the following figures were obtained.

$\%H_2O_2$	Mol. Cond. of KCL at infinite dilution
100	65.5 0°C
90	66.0
35.5	71.5
22.2	75.8
water	81.5

The ionizing power = $\frac{\Lambda}{\Lambda_\infty}$ where Λ and Λ_∞ have the

Each curve in the above group of four represents the relationship between molecular conductivity and percentage of peroxide at same dilution. K C L is the electrolyte. The curve marked infinite dilution was drawn by analogy to the above-mentioned ones and was used in calculating the ionizing power of the aqueous solutions and pure peroxide.

significance already referred to. A comparison can now be made for $\frac{\Lambda}{\Lambda_{\infty}}$ between KCL in water and KCL in the peroxide solutions at the same dilution.

Dilution 10

$\%H_2O_2$	$\frac{\Lambda}{\Lambda_{\infty}}$	Ionizing Power
100	$\frac{55.5}{65.5}$	.848
90	$\frac{56,5}{66.0}$	.856
35.5	$\frac{59.2}{71.5}$	.830
22.2	$\frac{65.7}{75.8}$	.868
water	$\frac{71.5}{81.5}$	.877

Dilution 50

$\%H_2O_2$	$\frac{\Lambda}{\Lambda_{\infty}}$	Ionizing Power
100	$\frac{61.8}{65,5}$	.945
90	$\frac{62.7}{66.0}$	.952
35.5	$\frac{66.3}{71.5}$	.928
22.2	$\frac{71.2}{75.8}$	.941
water	$\frac{76}{81.5}$	.932

Dilution 100

% H_2O_2	$\frac{\Lambda}{\Lambda_\infty}$.	Ionizing Power
100	$\frac{62.6}{65.5}$	.957
90	$\frac{63.5}{66.0}$	.962
35.5	$\frac{67.4}{71.5}$	.942
22.2	$\frac{72.8}{75.8}$	.961
water	$\frac{77.6}{81.5}$	.955

The approximate ionizing power so calculated leads one to the conclusion that the degree of dissociation of strong electrolytes is about the same as in water. This point of view is fully substantiated by the lowering of the freezing point of salts dissolved in pure hydrogen peroxide.

Certainly there is no evidence to show that the higher dielectric constant of the peroxide solutions markedly increases the ionizing power. In point of fact it is to be noted that in all three cases i.e. for dilutions, 10, 50 and 100 a minimum value for the ionizing power is obtained for the 35% solution whose dielectric constant is highest. Due, however, to the approximate character of the data definite statements cannot be made until more accurate values are obtainable. The only conclusion which appears justifiable is that due to the abnormally high values of the dielectric constant of water, hydrogen peroxide and its aqueous solutions. The ionizing power of these solvents is high and of a comparable magnitude.

THE ACIDITY OF HYDROGEN PEROXIDE

It was always noted that irrespective of the degree of purity that could be obtained, that solutions exhibited an acid reaction towards litmus paper. Other investigators have described hydrogen as a weak acid and it is interesting to see just to what extent this is true.

On comparing the hydrogen ion concentration of water, hydrogen peroxide, carbonic and basic acids, the following results are obtained:

Substance	
H_2O	$.8 \times 10^{-7}$
H_2O_2	$.4 \times 10^{-5}$
Boric acid	$.8 \times 10^{-4}$
Carbonic Acid	6×10^{-4}

The H^+ ion value for peroxide was obtained on the presumption that the specific conductivity was 2×10^{-6} and that the sum of the ionic conductances of H^+ and HO_2^- ions at infinite dilution was approximately the same as water viz. 487. As, however, the measurements were carried out in a glass vessel the true conductivity may be considerably lower. All that the above table is designed to show is that hydrogen peroxide is a very weak acid, even on making comparisons with boric and carbonic, which are known to typify weak acids.

SUMMARY

The physical constants of hydrogen peroxide are probably of most interest when compared and contrasted to those of water. Due to the fact that the constants described and discussed belong to distinct branches of physical chemistry it was considered best to deal with them under separate headings referred to as Section 1, 11, and 111.

In the first place, the value of any constant depends on two things, the purity of the material under investigation and also the accuracy of the measurements. Few substances offer greater difficulty in this respect, for both the purification and subsequent measurements must be carried out under such conditions as will ensure minimum decomposition.

Due to this complicating factpr of decomposition, a detailed account of how the process of purification was carried out seemed pertinent. It has been maintained that each organic stabilizer if present must be treated in a specific fashion depending on its chemical nature and its effect on the peroxide solution. In the case of inorganic stabilizers or impurities these are satisfactorily removed by distillation in slightly alkaline solution.

As one of the criteria of purity a re-determination of the melting point was considered advisable. The value -.90 appears to be more correct than that previously determined by Maass and Hatcher. The reasons for this are discussed in Section 1.

The density determinations differ slightly from Maass and Hatcher's values. Decomposition of Hydrogen peroxide in the dilatometer made necessary the correction of the reading for the volume of oxygen liberated. 1.4649 is considered to be the correct value at 0°C.

The final part of section 1 has to do with the partition of hydrogen peroxide between ether and water. No data is available from other sources above 30% peroxide. The results in section 1, however, cover the whole range of concentrations. It was also found that the simple application of the distribution law was impossible as no constancy in the partition is to be noted, even for dilute solutions. When however the state of aggregation of hydrogen peroxide is taken into consideration, a reasonable agreement to constancy is obtained. The value of the distribution law in this case then, appears to be that a qualitative relationship exists between the nature of the solvent and the state of aggregation of the peroxide dissolved in it.

Section 11 is devoted to the dielectric constant of peroxide and water. The physical and chemical significance of this constant was discussed and the theory as developed by Debye given.

The apparatus for measurement of the dielectric constants of liquids has two distinguishing characteristics from those employing the resonance principle. Flexibility in design makes possible measurements at different frequencies, and secondly, the type of cell used permitted accurate determinations without the necessity of correcting for lead or end effects in the condenser.

As to the values obtained, those for water agree reasonably well with previous investigators. So far as is known, no accurate value has been obtained for pure hydrogen peroxide. The measurements made with it and its aqueous solutions show that the value is higher than water. For 100 per cent peroxide it is 89.2, passing through a maximum for a 35 per cent solution of 120 and gradually dropping to 84 corresponding to water at 0°C.

By making use of the refractive index measurements and those of the dielectric constant, the electrical moments were calculated, both for water and aqueous solutions of peroxide. It is concluded that the high degree of association in the case of water and pure peroxide, annihilates the permanent moment of the single molecule and that in solution the effect of the fields of force around both the solvent and solute molecules give rise to moments of comparable magnitude to those of either water or pure peroxide. Finally, a structural formula is given based on modern valence concepts.

In section 111 a method for the accurate measurement of conductivity of salts in peroxide was discussed. Polarization and decomposition at the electrode are eliminated. The values obtained in solution using K CL as an electrolyte indicate that the ionization is of the same order as water. The results were discussed from the standpoint of the dielectric constants of the media but no quantitative considerations could at present be drawn from them.

In conclusion, it appears correct to consider hydrogen peroxide as a highly associated liquid possessing an ionizing power comparable to that of water. In contrast its energetic oxidizing properties, and ease of decomposition indicate the effect of the addition of an extra oxygen atom to an extremely stable molecule like water.

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